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Low-Volume Pulsed Hydrogen Biosparging

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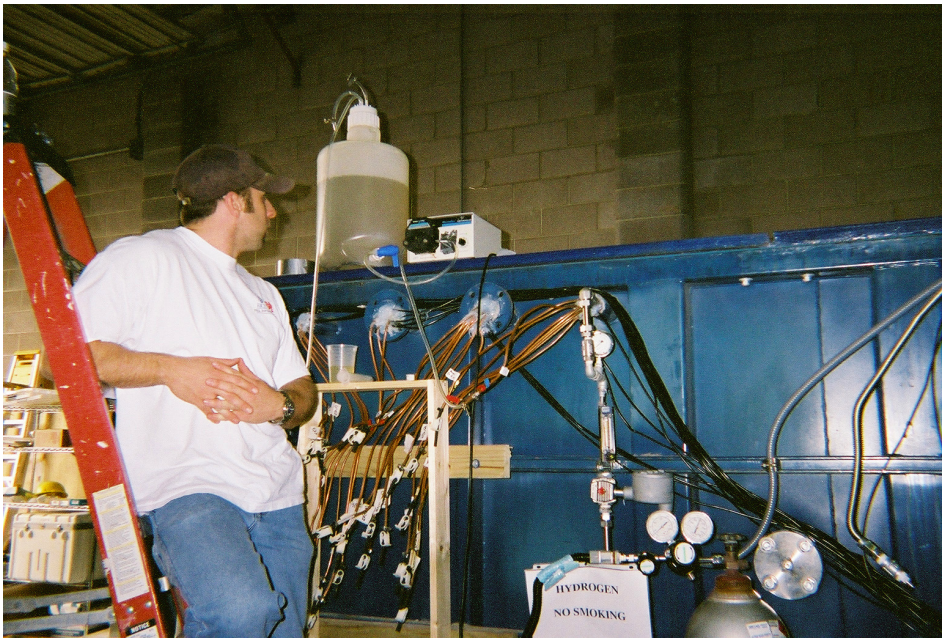

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Groundwater Services, Inc., Houston, TX

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FINAL REPORT FOR LOW-VOLUME PULSED BIOSPARGING OF HYDROGEN FOR BIOREMEDIATION OF CHLORINATED SOLVENT PLUMES

Groundwater Services, Inc., Houston, TX

1.0 EXECUTIVE SUMMARY

As a result of the widespread use as degreasers, solvents, and dry-cleaning agents, chlorinated solvents, such as perchloroethylene (PCE) and trichloroethylene (TCE), are among the most prevalent of groundwater contaminants found at DoD sites. These compounds commonly exist as dense nonaqueous-phase liquids (DNAPLs) and thus can serve as long-term, continuing sources of contamination as they slowly solubilize into moving groundwater. Laboratory studies have shown hydrogen is an effective electron donor for stimulating the biological reductive dechlorination of chlorinated solvents (Holliger et al., 1993; DiStefano et al., 1992; Maymo-Gatell et al., 1995; Gossett and Zinder, 1996; Smatlak et al., 1996; Hughes, Newell, and Fisher, 1997; Carr and Hughes, 1998). One method that has the potential to effectively deliver hydrogen in contaminated groundwater is low-volume pulsed hydrogen biosparging (LVPB-H2).

The purpose of this research was to investigate the efficacy of bioaugmentation and hydrogen biosparging for stimulating reductive dechlorination of a simulated dissolved PCE plume and a PCE DNAPL source area. In addition, hydrogen gas delivery radius and persistence were examined under different conditions to shed light on suitable sparging conditions in the field.

The experimental approach was to utilize the Experimental Controlled Release System (ECRS), developed by the Advanced Applied Technology Demonstration Facility (AATDF) to facilitate the testing and development of innovative remediation technologies. The ECRS included a 5400 gallon tank, which served as the reaction tank where the contaminated aquifer was simulated. Prior to filling the tank with sand, two well screens (0.5 ft of 2”I.D. 10 slot stainless steel well screen*)* were installed in the tank to serve as sparge wells.

The first experiment examined hydrogen biosparging for stimulating reductive dechlorination of a dissolved PCE plume. PCE-laden water at 1.6 mg/L was pumped through the tank at approximately 0.1 gpm (an 11-day hydraulic retention time). The effluent was treated with activated carbon to remove chlorinated constituents and ethene prior to being circulated to the head of the tank. Hydrogen gas was metered into the tank using a rotameter, and the flow was controlled with a solenoid valve on a timer. The ECRS tank was equipped with over 60 copper sampling lines for aqueous sampling and 46 time domain reflectometry (TDR) waveguides. TDR measured the % moisture by measuring the rate at which an electromagnetic wave is propagated. Changes in % moisture were converted to changes in % gas saturation, which were used to map hydrogen gas distribution.

The simulated aquifer was inoculated with 30 gallons of a mixed dechlorinating culture from Rice University. In total, 4.3 grams of bacteria were added to the simulated aquifer. Within 9 days, reductive dechlorination was observed. Furthermore, for 110 days the rate and extent of reductive dechlorination generally increased with time, suggesting bacterial growth. Bacterial activity was maintained over the one-year experimental period.

The maximum dissolved hydrogen delivery radius when the hydrogen was sparged for a 1 minute at 0.45 scfm was seven feet as measured using SF_6. TDR yielded a smaller radius of 2 ft, because it measured percent gas saturation, a less sensitive measurement approach. Although the hydrogen delivery radius is a function of the aquifer matrix, sparging conditions, and depth of the sparge point, the hydrogen delivery radius is expected to increase with increasing depth of the sparge point at actual field sites to a maximum of about 10 ft (Cannata et al., 2000).

Three weeks after bioaugmentation, the hydrogen persisted for 4 days (as determined by dissolved hydrogen) and 2 days (as determined by TDR) when sparged for 1 minute at 0.45 scfm. Four and a half months later, using more sparge gas (1 min at 1.59 scfm), the hydrogen lifetime was shorter, presumably due to a larger bacterial population. Although the persistence of hydrogen in a field application will be site-specific, this work indicated that sparging intervals between twice a week and once a day were effective for dissolved phase plumes. Hydrogen persistence is expected to decrease as the bacterial populations grow.

In the six-month dissolved PCE experiment, 82% of the total PCE entering the tank was removed, and 78% was removed by biotransformation in the 18-ft reaction zone using only one sparge well. Only 2% of the chlorinated constituents volatilized during sparging, indicating that volatilization was not a major loss mechanism for PCE or its reductive dechlorination products at the groundwater flow velocity (600 ft/yr) employed in this experiment. Vinyl chloride did not accumulate to levels approaching the mean influent PCE concentration of 9.7 uM. Some vinyl chloride may have been lost via other degradation processes such as anaerobic oxidation.

Methanogenesis, acetogenesis, sulfate reduction, and high hydrogen gas saturations did not prevent reductive dechlorination. Reductive dechlorination rate constants using hydrogen biosparging were 2-3 orders of magnitude higher than those determined for field sites undergoing rapid natural attenuation. However, only 2.5% of the added hydrogen was used for reductive dechlorination, indicating that other bacterial processes are a major sink for hydrogen.

In a second experiment, 1 L of DNAPL was emplaced in three locations near the first sparge point. Water was circulated through the ECRS at 0.1 gpm. The effluent was passed through activated carbon prior to circulation to the head of the tank.

The second experiment demonstrated that some reductive dechlorination was possible within 1.5 ft of a PCE DNAPL source. Three to four months were required before significant reductive dechlorination was observed. This may have been due to the lag time required for the bacteria to grow to sufficient numbers to effect significant transformation, insufficient electron donor, and/or high temperatures during this phase of the experiment. The final effluent composition was 12% PCE, 25% TCE, 61% cis-1,2-dichloroethylene (cDCE), 2% vinyl chloride (VC), and 0.1% ethene (ETH), indicating that hydrogen was effective at transforming PCE at high concentrations found within 10 feet of a DNAPL source. Low levels of vinyl chloride and ethene may have been due to short residence times or inhibition of cDCE dechlorinating bacteria by high levels of PCE and TCE. Declining temperatures may have been a factor in the improved performance near the end of the experiment.

Enhanced DNAPL dissolution was not observed in this experiment. This result was likely due to low rates of biodegradation that were sustained in the ECRS during most of the DNAPL source biodegradation experiment.

2.0 INTRODUCTION

As a result of the widespread use as degreasers, solvents, and dry-cleaning agents, chlorinated solvents, such as PCE and TCE, are among the most prevalent of groundwater contaminants found at DoD sites. These compounds commonly exist as dense nonaqueous-phase liquids (DNAPLs) and thus can serve as long-term, continuing sources of contamination as they slowly solubilize into moving groundwater. When left untreated, these compounds tend to persist in the environment, generating large contaminant plumes. Laboratory studies have shown that the addition of hydrogen as an electron donor is effective in stimulating the biological reductive dechlorination of chlorinated solvents (Holliger et al., 1993; DiStefano et al., 1992; Maymo-Gatell et al., 1995; Gossett and Zinder, 1996; Smatlak et al., 1996; Hughes, Newell, and Fisher, 1997; Carr and Hughes, 1998). The challenge in transferring this technology to the field is to effectively distribute and mix the hydrogen with the contaminants in situ.

One method that has the potential to effectively deliver hydrogen in contaminated groundwater is low volume pulsed hydrogen biosparging (LVPB-H2). Pulsed biosparging has the potential to more effectively deliver hydrogen than continuous sparging (Rutherford and Johnson, 1996) and has been used successfully for oxygenation in other bioremediation schemes (Salanitro et. al, 2000). Furthermore, hydrogen's high diffusivity aids its diffusion, improving its distribution in the subsurface and increasing the rate of reductive dechlorination.

Hydrogen biosparging represents an innovative, cost-effective technology for the management of chlorinated solvent plumes because of hydrogen's low cost and its ability to promote rapid dechlorination. The proposed technology may be implemented in various configurations for active plume remediation or passive barriers to plume migration.

3.0 BACKGROUND LITERATURE

3.1 Hydrogen for Stimulation of Reductive Dechlorination

Although chlorinated solvent compounds are known to undergo natural (unassisted) biological dechlorination under anaerobic conditions in the field (Gossett and Zinder, 1996; Wiedemeier, Rifai, Newell, and Wilson, 1999), the rate of natural dechlorination is often limited by the lack of adequate quantities of electron donor. Hydrogen is now widely recognized as a key electron donor required for the biologically-mediated dechlorination of chlorinated compounds (Holliger et al., 1993; DiStefano et al., 1992; Maymo-Gatell et al., 1995; Gossett and Zinder, 1996; Smatlak et al., 1996; Hughes, Newell, and Fisher, 1997). Hydrogen is produced in the subsurface by the fermentation of a wide variety of organic compounds including anthropogenic compounds, such as petroleum hydrocarbons and natural organic matter.

Direct hydrogen addition, where hydrogen gas is delivered to the subsurface, is a patented in-situ bioremediation technology for chlorinated solvent plumes that is under development (Hughes, Newell, and Fisher - U.S. Patent 5,602,296, February 11, 1997). This technology represents an extension of naturally-occurring dechlorination processes, because the rate-limiting biological step (i.e., slow fermentation of organic electron donors) is eliminated by providing naturally-occurring dechlorinating bacteria with substantive quantities of hydrogen.

In this process, hydrogen acts as an *electron donor* and halogenated compounds such as chlorinated solvents act as *electron acceptors,* becoming reduced in the reductive dechlorination process. Reductive dechlorination reactions are shown below for PCE, TCE, cis-1,2-dichloroethylene (cDCE), and vinyl chloride (VC):

$$PCE + H_2 \Rightarrow TCE + H^+ + Cl^-$$
$$TCE + H_2 \Rightarrow cDCE + H^+ + Cl^-$$
$$cDCE + H_2 \Rightarrow VC + H^+ + Cl^-$$
$$VC + H_2 \Rightarrow ethene + H^+ + Cl^-$$

Although reductive dechlorination has the potential to generate vinyl chloride, vinyl chloride can be degraded by a variety of mechanisms, including aerobic oxidation (Vogel and McCarty, 1985) and oxidation by ferric iron reduction (Bradley and Chappelle, 1996). A recent Air Force Center for Environmental Excellence chlorinated solvent plume database study found that vinyl chloride plumes were generally shorter than cDCE and TCE plumes at chlorinated solvent release sites, implying rapid degradation of vinyl chloride (Aziz et al., 1999).

An additional benefit of hydrogen biosparging technology is an increase in biological dechlorination efficiency over time. Both laboratory studies and kinetic models show that populations of dechlorinating microorganisms in natural systems will be more successful at competing for hydrogen in a hydrogen-rich environment (i.e., concentrations above nano-molar concentrations observed in natural plumes, where hydrogen is being generated only by fermentation) (Carr and Hughes, 1998). This result can be attributed to the dechlorinators having: i) a higher yield, and ii) a high maximum specific growth rate. In a hydrogen-rich

environment, the population of dechlorinators will increase with time, making bioremediation more efficient over time. This trend was demonstrated in laboratory column studies that showed the PCE half-life decreasing from 16.1 h after 98 days of column operation to 7.8 h after 129 days. Therefore, dechlorination at higher hydrogen partial pressures was not impacted by competition for hydrogen by other H_2-utilizing microorganisms.

Direct hydrogen addition is also simpler and more efficient than addition of liquid, fermentable substrates (such as methanol, toluene, lactate, benzoate, etc.) for enhancing biodegradation of chlorinated solvents in the subsurface. The disadvantage of these liquid substrates is that they must undergo intermediate fermentation to produce the hydrogen necessary for dechlorination. As a result, as much as 70% of the process energy goes to the production of acetate rather than hydrogen. Furthermore, these liquid substrates must be mixed with the groundwater in the contaminated zone, an undertaking requiring pumping, surface treatment, and injection. With hydrogen biosparging, no pumping or surface treatment is required. The simplicity of the technology gives hydrogen biosparging a significant advantage over liquid fermentable substrates.

3.2 Low Volume Pulsed Biosparging (LVPB-H_2) for Delivering Hydrogen

A key factor in the potential effectiveness of hydrogen biosparging is the efficient delivery of hydrogen. Sparging is a remedial technique whereby a gas (typically air) is injected into the saturated zone, forming gas channels between the injection point and the unsaturated zone (Johnson *et al*., 1993). Unlike a conventional air sparging system that removes volatile organic compounds primarily by stripping at flow rates in the 2 to 16 standard cubic feet per minute (scfm) range, low pressure air biosparging introduces a smaller flow of gas (e.g., < 3 scfm) to stimulate in-situ biodegradation processes while minimizing volatilization (Billings et al., 1995; Nyer and Suthersan, 1993).

Over the past few years in air sparging practice, it has been discovered that pulsing the gas flow results in greatly improved contaminant mass removal rates (Clayton *et al*., 1995; McKay et al., 1996). For example, Clayton *et al*. (1995) observed mass removal rates to increase by a factor of 3-5 when a pulsed air-sparging regime, using a pulse frequency between 12 and 24 hours, replaced continuous air sparging. Increased groundwater mixing was cited as the reason for increased mass removal. Physical groundwater displacement and groundwater movement resulting from capillary pressure gradients were identified as the two most likely and effective mechanisms for the increased mixing.

Hydrogen biosparging builds on the knowledge gained from air sparging research and experience. It is also potentially a more efficient hydrogen delivery approach than the liquid delivery/fermentation options discussed above. In hydrogen biosparging, hydrogen is delivered to groundwater by a gas delivery system based on short-duration gas injections at low frequencies. The short duration ensures minimal gas loss to the vadose zone, and the low frequency is possible because residual hydrogen gas trapped in the aquifer pores continues to dissolve into the flowing groundwater between gas injections. The low cumulative volume and low frequency of gas injections makes the economics of LVPB-H2 very favorable.

3.3 Previous Work

3.3.1 Laboratory Experiments

Laboratory column studies sponsored by Groundwater Services, Inc. and conducted by Dr. Hughes at Rice University have shown the potential for directly adding hydrogen as an electron donor to aid in the biological reduction of chlorinated compounds (Carr and Hughes, 1998). In Hughes' laboratory system, hydrogen supported the transformation of PCE to reduced end products. Results from three column experiments indicated that PCE degradation was extremely rapid, ranging from 0.12 mg/L/hr to 0.46 mg/L/hr. PCE degradation rates were also found to improve with time as the bacterial population grew. Dechlorination was not impacted by competition for electron donor at high hydrogen partial pressures by other hydrogen-utilizing microorganisms, particularly methanogens (Carr and Hughes, 1998).

3.3.2 Field Tests

Following laboratory studies, a project to field test the applicability and feasibility of direct hydrogen addition using both dissolved and sparged hydrogen was initiated by the Technology Transfer Division, Air Force Center for Environmental Excellence (AFCEE/ERT). The current test program under Contract No. F41624-97-C-8020 includes long-term (18 month) pilot tests at various Air Force installations. Results from a low-volume pulsed hydrogen sparging pilot test at Cape Canaveral Air Station, Florida also showed biological dechlorination as shown in the tables on the next page (Newell et al., 2000). Sampling events were conducted prior to sparging (baseline) and at one week, four month, 12 month, and 18 month intervals. Approximately 130 scf of a 49% hydrogen, 49% helium, and 2% SF_6 gas mixture was pulsed into each of the three sparge points (located on 12-ft centers) on the first day of sampling (2/7/99). After the first day, smaller 1-minute "maintenance" pulses consisting of 15-20 scf of research grade hydrogen gas were added to each sparge point once per day. One well was sparged with nitrogen to serve as a control.

For the purpose of more easily comparing concentrations over time, four groups of wells were evaluated using geometric means. The wells were selected based on the distance to the hydrogen and nitrogen sparge wells.

1. GROUP A. HYDROGEN TEST ZONE - CLOSE (Geometric Mean of 6 CLOSE Sampling Pts in H_2 Test Zone, 3-6 ft horizontally from sparge points)

2. GROUP B. HYDROGEN TEST ZONE - MIDDLE (Geometric Mean of 3 Downgradient Sampling Pts in H_2 Test Zone, ~15 ft from sparge points)

3. GROUP C. NITROGEN CONTROL ZONE - MIDDLE (1 Downgradient Sampling Points in N_2 Control,15 ft. from sparge pt)

4. GROUP D. NATURAL ATTENUATION CONTROL ZONE - MIDDLE (Geometric Mean of 2 Sampling Points in N_2 Control, 20 ft from sparge pt)

After 18 months there was a large decrease in TCE, cDCE, and VC relative to the nitrogen control. Excessive methane production was not observed in the hydrogen delivery zone and no breakthrough of hydrogen gas to the surface was detected during this initial sparging event (vadose zone thickness: 5 ft). Data acquired from the site from the 12-month sampling event (March 2000) showed the system had been successful at delivering gas (as indicated by the helium tracer) up to 15 feet away from the sparge points, with concentrations of the tracer near saturation in a zone 6 feet away from the sparge points.

TCE CONCENTATION (mg/L)						
Group of Wells	BASELINE	AFTER 1 WEEK	AFTER FOUR MONTHS	AFTER 12 MONTHS	AFTER 18 MONTHS	% CHANGE OVER 18 MONTHS
A. H_2 Test Zone – Close	14.1	8.1	0.5	1.1	0.15	- 99 %
B. H_2 Test Zone – Middle	6.7	-	1.8	2.1	1.37	- 80 %
C. N_2 Control Zone – Middle	<0.55	-	<0.1	0.1	<0.25	ND
D. N.A. Control Zone - Middle	21	-	27	36	20	- 5 %

c-DCE CONCENTATION (mg/L)						
Group of Wells	BASELINE	AFTER 1 WEEK	AFTER FOUR MONTHS	AFTER 12 MONTHS	AFTER 18 MONTHS	% CHANGE OVER 18 MONTHS
A. H_2 Test Zone – Close	237.1	239.3	88.2	64.4	13.16	- 94 %
B. H_2 Test Zone – Middle	244.9	-	183.7	153.9	101.21	- 59 %
C. N_2 Control Zone – Middle	21.0	-	27.0	36.0	20.0	- 5 %
D. N.A. Control Zone - Middle	169.4	-	158.7	142.8	124.38	- 26 %

	VINYL CHLORIDE CONCENTATION (mg/L)					
Group of Wells	BASELINE	AFTER 1 WEEK	AFTER FOUR MONTHS	AFTER 12 MONTHS	AFTER 18 MONTHS	% CHANGE OVER 18 MONTHS
A. H_2 Test Zone – Close	39.5	21.6	21.1	28.2	2.49	- 94 %
B. H_2 Test Zone – Middle	42.1		48.0	49.9	48.23	+15 %
C. N_2 Control Zone – Middle	21.0	-	29.0	<2.5	17.0	- 19 %
D. N.A. Control	21.4		20.7	26.2	23.64	+ 10 %

4.0 TECHNICAL OBJECTIVES

Although hydrogen biosparging has been tested in the field, a number of questions about how to design and implement LVPB-H_2 systems remained. The following questions were addressed in this study:

1. How much hydrogen gas can be pulsed into the subsurface safely?
2. What is the rate and extent of PCE reductive dechlorination using hydrogen delivery via LVPB-H2 and bioaugmentation?
3. What is the effective delivery radius of a LVPB-H_2 pulse away from the sparge point, under different injection conditions?
4. How long does residual hydrogen gas persist in the groundwater ?
5. How does hydrogen biosparging affect the rate and extent of dechlorination in source areas?

Breakthrough experiments were important to determine how much hydrogen could be added to the ECRS under safe conditions. Delivery radius studies were useful for determining the pulse duration to get sufficient distribution of hydrogen away from the injection well. The radius of influence provided information for sparge point spacing needed to estimate well installation costs. The lifetime of trapped residual hydrogen gas was needed to determine the optimal pulse frequency, which can drive the process economics at many sites. The rate at which reductive dechlorination occurs was important so that clean-up times could be estimated.

The ultimate goal of this work was to develop an in-situ remedial technology for the biodegradation of dissolved chlorinated solvents in contaminated groundwater. LVPB-H2 was used to deliver a concentrated source of hydrogen (i.e., electron donor) to stimulate the rate and extent of chlorinated solvent reductive dechlorination. The experimental strategy was to utilize the Experimental Controlled Release System (ECRS) developed by the Advanced Applied Technology Demonstration Facility (AATDF) to facilitate the testing and development of innovative remediation technologies.

5.0 TECHNICAL APPROACH

5.1 System Overview

The Experimental Controlled Release System (ECRS) was developed to provide a means to quantitatively assess the effectiveness of various remediation techniques involving saturated or unsaturated subsurface conditions on a pilot scale of operations. Primary ECRS components include i) a process equipment skid containing an air compressor, water pumps, controls, and instrumentation; ii) a 5400-gallon rectangular tank (18 ft long, 7 feet wide, and 6 feet tall) equipped with sampling ports; and iii) ancillary water tanks.

The 5400 gallon tank served as the reaction tank where the contaminated aquifer was simulated. A three-screen manifold was installed at the upgradient and downgradient ends of the tank to aid in the distribution of the incoming and outgoing water. Prior to filling the tank with sand, two well screens (0.5 ft of 2"I.D. 10 slot stainless steel well screen*)* were installed in the tank to serve as sparge wells. The wells were fed gas from the bottom using a ¾-inch stainless steel line and the screens were capped at the top. The locations of the sparge wells are shown in Figure 1. The sparge well positioned at the (x,y,z) coordinate (6,3.5,0.5) was the main sparge well used for biosparging throughout the experiments. The second sparge well was used only in the DNAPL experiment.

Before beginning experimentation, the ECRS tank was filled with clean, fine commercial grade masonry sand obtained from General Terrazzo, Houston. The mean sand characterization data can be found in Table 1. The grain size distribution is shown in Figure 2.

5.2 Packing and Degassing of the ECRS Tank

The sand was added to the ECRS tank in 3-inch lifts using a front-end loader and compacted using manual and pneumatic compactors. The first upgradient foot and last downgradient foot of the tank were packed with a coarse sand to aid in the even distribution of the water. Two sheets of plywood were used to separate the coarse sand from the fine sand. The plywood sheets were advanced upward after each lift had been compacted. The tank was filled with sand to approximately 0.5 foot from the top of the tank.

As the sand was added, sampling tubing and time domain reflectometry (TDR) waveguides were installed at various locations and depths within the tank. Figure 1 shows the TDR waveguide locations. TDR was used to measure the soil moisture, which could be used to indirectly measure the gas saturation. TDR cables were directed horizontally along the layer and out a port in the side of the ECRS tank. The cables were labeled to identify their locations and the port was sealed with silicone caulking. The waveguides were connected to a multiplexer, which interfaced with a TRACE BE unit and laptop computer for data acquisition.

Sampling lines were also positioned as the ECRS tank was packed. Figure 3 shows the available sampling locations in the ECRS tank. Flexible copper tubing (1/4" I.D.) was used for the sampling tubing. The ends of the tubing were covered with a fine stainless steel mesh screen and secured with a stainless steel hose clamp to prevent fine soil particles from entering

with the sample. The lines were positioned horizontally at the sampling level. The exact position of the sampling point was secured by burying the sampling line 1" into the sand. The copper sampling lines were directed out a side port near the top of the ECRS tank and labeled to identify their position.

Prior to flushing water through the tank, the ECRS tank was flushed with carbon dioxide to remove trapped air. Carbon dioxide was simpler than air to subsequently remove from the tank, because of its higher solubility in water.

5.3 ECRS Operation

During the dissolved PCE experiment, PCE-laden water at a mean concentration of 1.6 mg/L was pumped to the front end of the tank and distributed within the tank using three interconnected well screens. Water was passed through the tank (from left to right) at approximately 0.1 gpm (600 ft/yr). This corresponded to a water retention time of approximately 11 days within the tank. The effluent was treated with activated carbon to remove chlorinated constituents and ethene prior to being circulated to the head of the tank.

Hydrogen gas was metered into the tank using a rotameter, and the flow was controlled with a solenoid valve on a timer. During and following hydrogen injection, the headspace was purged with nitrogen at 1 scfm for 20-45 minutes to remove any vinyl chloride or hydrogen that had built up in the headspace. The nitrogen purge was controlled by a solenoid valve and timer.

The ECRS tank was equipped with over 60 copper sampling lines for aqueous sampling and 46 time domain reflectometry (TDR) waveguides. TDR measured the % moisture by measuring the rate at which an electromagnetic wave was propagated. Changes in % moisture were converted to changes in % gas saturation, which were used to map hydrogen gas distribution.

Specific methodologies for each of the studies are outlined in Section 6.0.

6.0 PROJECT ACCOMPLISHMENTS

6.1 Helium Breakthrough Experiments

6.1.1 Objectives

The objectives of this phase of the work were to determine the amount of hydrogen that could be safely sparged into the ECRS tank and to determine the radius of influence of the sparge using time domain reflectrometry (TDR). The gas volume that yielded the greatest radius of delivery without significant breakthrough is also important for sparge point spacing and for optimizing gas use. This phase of the experiment provided an indication of the amount of gas that could be sparged prior to breakthrough and could be used to estimate whether the sparged gas concentration in the headspace would exceed the lower flammability limit for hydrogen.

6.1.2 Methodology

The ECRS tank was filled with 5 ft of water. Helium, as a surrogate for hydrogen, was sparged into the tank at flow rates ranging from 0.01 to 0.53 standard cubic feet per minute (scfm). With the tank uncovered, a 1' x 1' grid system was set up across the top of the tank using string. The flow rate of helium was increased until breakthrough occurred. With the cover off, the breakthrough time was determined, and breakthrough was photographed at each flow rate investigated. Breakthrough was defined as greater than 2 seconds of continuous off-gassing.

Once breakthrough volumes were determined, gas was sparged into the tank for a period less than the breakthrough time for a given flow rate and TDR was used to map the resulting distribution of gas in order to estimate a delivery radius.

6.1.3 Results - Safe Injection Volumes

The breakthrough volume and breakthrough time versus helium injection flow rate are shown in Figure 4. The breakthrough volume increased with increasing injection flow rate, while the breakthrough time decreased with increasing flow rate. A photograph showing a typical breakthrough pattern is shown in Figure 5. The breakthrough pattern was diffuse and covered a 2 to 2.8 ft radius around the sparge point, depending on the injection flow rate, as reported in Table 2.

The key determinant to the safety of the injection was the concentration of helium in the headspace. The maximum helium concentration was estimated by assuming that 100% of the injected gas off-gassed. During operation with hydrogen, the ECRS tank was covered and sparged with nitrogen at 1-2 scfm for 15 minutes before and after the sparging of the hydrogen. Therefore, in calculating the helium concentration in the headspace, it was assumed that the gas in the headspace was well-mixed. The calculated helium concentrations for all of the conditions tested are shown in Table 2. All of the concentrations were well below 4% (v/v), the lower flammability limit for hydrogen. Therefore, all volumes of gas injected would be considered "safe" by this definition. Furthermore, the atmosphere in the tank during operation with hydrogen would be anaerobic, due to the deoxygenation of the incoming water and sparging of the headspace with nitrogen. The absence of oxygen was a further safety measure.

The limiting factor in determining the highest gas flow rate that could be used in the ECRS tank was the overburden pressure within the tank. Fluidization could occur at a total overburden pressure (soil column pressure + water pressure) of 4.4 psig for this system (Army Corps of Engineers, 1997). Table 2 presents the pressures measured for each of the flow rates tested. A flow rate of 0.53 scfm was the last flow rate tested because the pressure reached 2.7 psig (60% of the fluidization pressure).

6.1.4 Results – Delivery Radius

The second objective of this phase of the work was to determine the helium delivery radius over the range of flow rates investigated. Helium was injected at various flow rates and durations (typically <50% of the breakthrough time) as detailed in Table 3. Prior to each sparge, a baseline TDR measurement was taken. Upon completion of the sparge, TDR measurements were taken at 45 locations. TDR contours were plotted by taking the change in soil moisture between the before and after TDR measurements. A positive change indicated a decrease in soil moisture and an increase in gas saturation, while a decrease in the soil moisture indicated a decrease in the gas saturation. Table 3 summarizes the delivery radii as delineated at 0.05% change in soil moisture at the centerline of the tank where the sparge points are locate. TDR was effective for visualizing gas distribution and water displacement as a result of the gas injection. The delivery radius ranged from 3.25 to 4.25 ft for the conditions investigated.

6.1.5 Conclusions

The following are the conclusions from the helium breakthrough experiments:

1. All flow rates tested appeared to be safe for hydrogen operation, because of the low amount of gas added compared to the volume of gas in the headspace. In addition, the headspace would be sparged with nitrogen to dilute any hydrogen that volatilized and to maintain an anaerobic environment during the biodegradation experiments.

2. The maximum injection flow rate of 0.5 scfm was constrained by the estimated fluidization pressure of the sand, including a safety factor of 40%. Injection of gases at deeper intervals will permit higher injection flow rates and gas volumes in the field.

3. TDR was an effective way to indirectly visualize gas distribution and estimate the helium delivery radius. Over the range of flow rates tested, delivery radii varied from 3.3 to 4.3 ft.

4. Based on the results of these experiments, 0.5 scfm of hydrogen will be sparged for 1 minute during the biodegradation experiments. This volume (0.5 ft^3) should not yield an unsafe headspace environment (<0.5% v/v maximum hydrogen concentration for well-mixed headspace) and should provide a delivery radius of at least 3.5 feet.

6.2 Bacterial Culturing and Activity

6.2.1 Objective

The objective of culturing the bacteria was to provide sufficient active biomass to bioaugment the ECRS tank for the experiments involving reductive dechlorination.

6.2.2 Methodology

The bacterial consortium used for bioaugmentation was cultured at Rice University in a 30-gallon high-density polyethylene bioreactor. The tank was equipped with ports for injection of nutrients, pH control, PCE addition, liquid sampling, recycling the contents of the bioreactor, and headspace analysis. The reactor was inoculated with a stock of rapidly dechlorinating microorganisms that had been fed methanol and PCE for a period of eight years. The system was operated as a fed-batch reactor for 6 months with routine additions of PCE and lactate.

Periodically, biomass samples were taken from the reactors and subjected to a 48-hour microcosm activity analysis. Fifty milliliters of biomass from the 30-gallon reactors were added to 70-mL glass bottles, and the bottles were purged with H_2/CO_2. Aqueous and headspace samples were taken from the bottles and analyzed over 48 hours using GC/FID.

6.2.3 Results

The percent degradation of PCE observed in each microcosm assay during bioreactor operation is shown in Figure 6. Almost all the PCE in the aqueous phase was removed. To assess the extent of reductive dechlorination and to assess whether PCE had volatilized, the microcosm headspace gas was analyzed for PCE and its daughter products. As shown in Figure 7, no PCE (and therefore no volatilization) was detected and the daughter products consisted mostly of vinyl chloride and ethene. The microcosm studies showed that the bacterial culture was active and capable of complete dechlorination to ethene.

6.3 Assessment of Background Bacterial Activity

6.3.1 Objectives

The objective of this study was to determine if the sand used to pack the ECRS tank had bacteria with dechlorinating activity to determine the ultimate effectiveness of bioaugmentation.

6.3.2 Methodology

Anaerobic microcosms were set up with sand used in the ECRS tank. Twenty milliliters of water spiked with 100 mg/L of lactate and 4 mg/L of PCE were added to a 70 mL bottle containing 50 g of soil. Sixteen microcosms were set up and two microcosms were sacrificed and analyzed every two weeks.

6.3.3 Results

No dechlorination occurred, indicating no or very few dechlorinating bacteria in the ECRS tank sand (Adamson et al., 2003). Therefore, any biodegradation occurring during the ECRS tank experiments was attributed to the added bacterial culture.

6.4 Bioaugmentation

6.4.1 Objective

The objective of this phase of the research was to demonstrate significant reductive dechlorination following bioaugmentation of the ECRS tank with a dechlorinating culture. This objective represented a GO/NO-GO decision point.

6.4.2 Methodology

Prior to adding the dechlorinating culture to the ECRS tank, anaerobic conditions were established. Acetate was added to the incoming water at a concentration of approximately 30 mg/L and PCE was metered into the system to achieve a mean concentration of 1.6 mg/L in the influent. Acetate served as a source of carbon for the bacteria as the Rice University culture does not use acetate as an electron donor (J. Hughes, personal communication). After 2 weeks, anaerobic conditions were established as evidenced by a dissolved oxygen concentrations of <0.5 mg/L in the effluent. No reductive dechlorination daughter products were seen in the effluent prior to bioaugmentation, confirming the results of the column study that showed no native dechlorinating activity.

On February 18, 2002, the ECRS tank was bioaugmented with the culture from Rice University. The culture was transported in carboys under nitrogen from Rice University to Groundwater Services' pilot laboratory facility housing the ECRS. The ECRS tank was sparged with hydrogen each day for 1 minute at 0.45 scfm to provide ample electron donor. The culture was pumped at approximately 1-3 gallons/hour using a peristaltic pump into 6 different locations near the primary sparge point as shown in Figure 8. The bioaugmentation was conducted over three afternoons. In total, 30 gallons of culture at a VSS of 38 mg/L, or 4.3 grams of bacteria, were added to the tank.

6.4.3 Results

Within 9 days, cDCE, a daughter product of reductive dechlorination, was observed in the effluent (Figure 9). After 11 days, TCE was observed in the effluent. The continued presence of these constituents demonstrated that significant reductive dechlorination had occurred in a very short time frame. Furthermore, the percentage of daughter products relative to PCE continued to increase for the first 3.5 months, indicating growth of the bacterial population. These results demonstrated that the bioaugmentation had been a success and that further reductive chlorinated studies with dissolved and free phase PCE would proceed.

6.4.4 Conclusions

1. Rapid onset of reductive dechlorination after bioaugmentation was observed.
2. The rate and extent of reductive dechlorination increased with time, suggesting bacterial growth.

6.5 Reductive Dechlorination Dissolved Phase Study

6.5.1 Objectives:

The objective of this study was to determine the rate and extent of reductive dechlorination using low-volume pulsed hydrogen biosparging.

6.5.2 Methodology

a. ECRS System Operation

The ECRS system was operated with recycle with a flow rate of 0.1 gpm. This corresponded to a hydraulic retention time of 11 days. Chlorinated constituents in the effluent were removed using granulated activated carbon prior to being circulated to the head of the tank. A concentrated solution of PCE was metered into the incoming water to achieve a mean concentration of 1.6 mg/L. Acetate was added periodically at concentrations between 10 and 30 mg/L.

b. Monitoring

Approximately twice weekly, the pH, dissolved oxygen, temperature, and oxidation-reduction potential (ORP) of the effluent were measured. Dissolved oxygen was measured using a YSI model 51B dissolved oxygen meter and probe, pH and temperature was determined using a 99/300 meter, and ORP was measured using an Orion Model 250A meter and probe. Dissolved oxygen, oxidation-reduction potential, and temperature were measured in-line using a flow through cell.

Three months after bioaugmentation, the influent and effluent were also monitored for ferrous iron and sulfate. Ferrous iron and sulfate were measured using colorimetric methods using Hach kits. The 1,10-phenathroline method (modified EPA method 8146, Hach kit model IR-18C) was used for ferrous iron analysis. Modified USEPA method 375.4 was used for the sulfate analysis.

c. Sampling Protocol

Prior to taking water samples for analysis, 300 mL of water (approximately twice the line volume) were discarded. 50-mL glass serum bottles, previously preserved with 2 drops of

concentrated sulfuric acid, were slowly filled to the 45 mL level with the aqueous sample and then immediately capped with a Teflon-lined septa and aluminum seal. The samples were put on ice or refrigerated until analysis. Samples from the influent and effluent were generally taken twice per week. Extensive sampling of the entire of the tank was performed five times over the course of the six-month experiment.

Gas samples from the headspace were collected using summa canisters. With the nitrogen gas flowing and after the hydrogen sparge, the summa canister was connected to the off-gas line. The valve was opened and a grab sample of the headspace was collected in the canister.

d. Analytical Methods

Aqueous phase samples were sent to Rice University for analysis. The analytes, methods, and preservatives are detailed in Table 4.

Chlorinated ethenes, ethene, and methane concentrations in experimental samples were determined using headspace analysis. Samples (100 µL) were injected directly into a gas chromatograph (GC) (Hewlett-Packard 5890) equipped with a flame ionization detector (FID) and a packed column (6 ft x 1/8 in. OD) containing 60/80 Carbopack B/1% SP-1000 (Supelco). The operating parameters of the GC have been previously described by Carr and Hughes (1998). Standards were prepared by adding PCE, TCE, and cDCE dissolved in methanol, and VC, ethene, and methane gases, all at known volumes, to serum 50-mL serum bottles containing 45 mL of deionized water.

Acetate was analyzed by first filtering aqueous samples (2.7 mL) through a syringe filter (0.2 µM) into a 10-mL screw-cap vial. To this sample, 0.3 M oxalic acid (0.3 mL) was added to yield a final concentration of 0.03 M oxalic acid. If not analyzed immediately, the sample was stored at 4°C until analysis. Samples were analyzed using a GC (Hewlett Packard 5890) equipped with a flame ionization detector (FID) that contained a glass packed column (2 m x 2 mm ID) containing 80/120 Carbopack B-DA*/4% Carbowax 20 M (Supelco). Using a syringe, a liquid sample (1 µL) was injected directly into the column. The operating parameters for the GC were as follows: oven temperature was 175°C, detector temperature was 200°C, and the injector temperature was 200°C. The flow rate for N_2 (carrier gas, 24 ml/min); air and H_2 were used as detector make-up gases.

Gas samples from the ECRS tank headspace were sent to Research Triangle Park Laboratory for analysis. The headspace gas was analyzed for chlorinated ethenes, ethene, ethane, and methane. Ethene, ethane, and methane were analyzed by GC/FID using EPA Modified Method 18. The chlorinated ethenes were analyzed using GC/MS using Method TO-14A.

e. Microcosm Studies

Forty-five milliliters of culture from the ECRS tank were collected from sampling point (14,3.5,2.5) using a sterile syringe. The culture was added to a sterile 60-mL bottle, which had previously been put under a vacuum. The volatile organics present in the culture were removed by purging the sample with nitrogen. Then, the bottles were dosed with 0.01 mM of cDCE or vinyl chloride and 2 mM of ferric iron. Two control microcosms were also studied. The first was

deioinzed water with 2 mM of ferric iron and 0.01 mM of vinyl chloride and the second was deionized water with 2 mM ferric iron and 0.01 mM cDCE. All conditions were run in duplicate.

f. Determination of Rate Constants

Rate constants were determined using the semi-analytical groundwater transport model, BIOCHLOR (Aziz et al. 2000). Data from the centerline of the tank (x, 3.5, 2.5) from Day 33, 76, 142, and 164 sampling events were used for calibrating the model. Biodegradation rate constants were adjusted until the model matched the observed data. A source of constant concentration was assumed.

The model parameters used are listed in Table 5. Porosity (n_e =0.35) was estimated using TDR. Soil bulk density (ρ=1.6 kg/L) and fraction organic carbon (f_{oc}=0.0012) were measured when the sand was characterized. Seepage velocity (v_s) was obtained using $v_s = Q/n_eA$, where Q was the average flow rate measured during the month before the sampling event and A is the cross sectional area of flow, equal to the height of water in the tank (4.9 ft) times the width of the tank (7 ft). The horizontal dispersion coefficient (α_x) was estimated from the graphical relationship between longitudinal dispersivity and scale of plume (18 ft in this case) provided by Gelhar *et al*. (1992). BIOCHLOR's default partition coefficient (K_{oc}) values for PCE, TCE, cDCE, and VC were used. The retardation factor used was an average of the calculated retardation factors of PCE, TCE, cDCE, and VC. The dimensions of the tank were used as the source thickness and width (where source thickness is the height of the tank and source width is the length of the tank perpendicular to flow). The initial concentration (C_o) of PCE used was an average of the influent concentrations from bioaugmentation (2/18/02) to the end of the experiment (8/5/02).

6.5.3 Results

a. VOC Effluent Data

To simulate a PCE dissolved groundwater plume, PCE was metered into the influent water to achieve a mean PCE concentration of 9.7 uM. Within 30-40 days after bioaugmentation, PCE concentrations were not detected in the effluent as shown in Figure 9. cDCE was the first daughter product to appear in the effluent only 14 days after bioaugmentation. TCE, vinyl chloride and ethene were detectable by the 17th day post-bioaugmentation. Therefore, evidence of complete dechlorination was observed as early as 17 days after bioaugmentation.

From day 64 through day 113, no PCE or TCE was found in the effluent (Figure 9). After 115 days, the concentration of PCE and TCE began to rise in the effluent. It was hypothesized that the system was either electron donor or carbon limited; so the amount of acetate added to the influent and the amount of hydrogen injected was increased. Acetate addition provided a source of carbon for growth, as it is not used by the dechlorinating culture as an electron donor for reductive dechlorination. By the end of the experiment, PCE and TCE concentrations had once again declined to less than 1 uM. Approximately 2-3 weeks were required to see the performance turn around.

cDCE demonstrated a different trend than PCE and TCE (Figure 9). It was produced very early (within 14 days) from the bioaugmentation and began to rise rapidly over the first 30 days. From day 30 to day 60, cDCE concentrations declined, presumably due to production of vinyl chloride (which increased over the same time period). For over two months, from days 60 to

day 120, no cDCE was measured in the effluent. Then, over the last 30-40 days, small concentrations (less than 1 uM) were observed in the effluent.

For the bulk of the experiment, vinyl chloride concentrations in the effluent remained relatively constant (Figure 9). Sixty days after bioaugmentation, vinyl chloride concentrations reached a maximum of 3 uM and then declined to 1-1.5 uM for the remainder of the experiment. Despite high conversion of PCE, TCE, and cDCE from day 64 to day 113, vinyl chloride did not accumulate. However, the ethene data indicated that vinyl chloride was not significantly reduced to ethene. Ethene was present in the effluent from day 22 to day 135 and then was not detectable for the remainder of the experiment. Between days 64 and 105, the composition of the effluent was more than 90% vinyl chloride but the actual concentration of vinyl chloride was only between 1 and 3 uM, significantly less than the mean PCE concentration of 9.7 uM entering in the influent. These results suggested that other mechanisms in addition to reductive dechlorination were responsible for the low concentrations of vinyl chloride during periods of high conversion of PCE, TCE, and cDCE.

b. Geochemical Parameters

Throughout the course of the experiment, methane concentrations increased gradually as seen in Figure 10. Despite increasing levels of methane, the concentration of methane had no impact on the extent of PCE removal (Figure 11) indicating that methanogenesis was not significantly inhibiting reductive dechlorination.

To account for the low vinyl chloride concentrations during periods of high PCE, TCE, cDCE conversion, aqueous samples of the influent and effluent were analyzed for ferrous iron and sulfate to determine if ferric iron and sulfate reduction were occurring. Iron reduction was consistently observed. The mean production of ferrous iron over the last 67 days of the experiment was 2.7 mg/L. Sulfate reduction was erratic, with reduction of sulfate concentrations between the influent and the effluent varying between 0 and 9 mg/L.

c. Microcosm Studies To Elucidate Other Mechanisms

Because iron reduction was clearly occurring within the ECRS tank and not all the degraded PCE could be accounted for by chlorinated ethene daughter products and ethene, microcosm experiments were conducted to determine if VC and cDCE were being degraded via anaerobic oxidation coupled to iron reduction. Over 300 hours, vinyl chloride degraded from 0.012 to 0.0085 mM, as shown in Figure 12. Over the same time period, in a separate microcosm, cDCE declined from 0.0093mM to 0.0078 mM, as seen in Figure 13. A deionized water control with no bacteria, 2mM ferric iron, and a nominal vinyl chloride concentration of 0.01 mM declined from 0.009 to 0.0075 mM (Figure 14). Despite some volatile losses, vinyl chloride anaerobic oxidation appeared to be a possible biodegradation mechanism. The results were less clear with the cDCE, as cDCE in the deionized water control declined from 0.009 to 0.008 mM over the same time period (Figure 15).

d. VOC Data from Large Sampling Events

In addition to monitoring the influent and effluent semi-weekly for PCE and reductive dechlorination daughter products, five additional large sampling events were conducted over the course of the experiment. For these events, samples were collected from approximately 20 different locations to characterize the chlorinated compound distribution within the tank. The concentration cross-sections for PCE through ethene for both the X-Y horizontal plane and the X-Z vertical plane can be found in Appendix A.

On February 18, 2002, before bioaugmentation, only PCE was evident in the tank (Figure A.1). No daughter products were present. These data confirmed earlier column studies, which indicated no native dechlorinating activity of the sand.

Sixty-two days after bioaugmentation on March 24, 2002 (Figure A.2), the concentration distribution had changed dramatically. Very little PCE and TCE were present within the tank. cDCE and VC were the constituents with the highest concentrations and ethene was observed in low concentrations upgradient of the sparge point (<0.1 uM) with increasing concentrations in the downgradient direction.

By May 6, 2002 (Day 105), no PCE was evident in the tank and there were only small areas where TCE and cDCE could be detected (Figure A.3). Vinyl chloride was the dominant constituent present, with generally increasing concentrations at increasing distances from the sparge point. Low levels of ethene were measured (<0.1uM) but the ethene was not as widely distributed as in the March 24th sampling event (Figure A.2).

By July 11, 2002 (Day 171), the system performance had declined and PCE and TCE were distributed throughout the tank at high concentrations (Figure A.5). PCE concentrations generally decreased with distance from the influent, while TCE concentrations generally increased due to carbon and/or hydrogen limitations. Moderate concentrations (i.e., 1-4 uM) of cDCE and 1-2 uM of vinyl chloride were evident downgradient of the sparge point. Trace amounts of ethene were still detectable within the tank.

By the end of the experiment on August 5, 2002, very low levels of PCE, TCE, and cDCE were present in the downgradient 50% of the tank, indicating improved performance over the preceding month after increased acetate addition (Figure A.5). Moderate levels (<4 uM) of vinyl chloride were present, particularly downgradient of the sparge point, while only trace levels of ethene were evident.

e. Methane and Acetate Data from Large Sampling Events

In addition to PCE and reductive dechlorination products, methane (and later acetate) were measured from multiple sampling points throughout the tank to map their respective distributions both spatially and temporally. Methane and acetate distributions were of interest because methanogens and acetogens can compete with dechlorinating bacteria for hydrogen. In addition, high methane concentrations indicated regions that were sufficiently reduced and more likely to be suitable for the reduction of the lesser chlorinated constituents providing sufficient hydrogen was present.

Prior to bioaugmentation on February 18, the methane concentrations were uniformly less than 0.1 mg/L throughout the tank, as shown in Figure B.1 in Appendix B. By the March 24th (Day 62)

sampling event, the area downgradient of the hydrogen sparge point was becoming increasingly methanogenic (Figure B.2). By May 6, 2002, methane levels were higher (Figure B.3) and the concentration distribution remained similar for the remainder of the experiment (Figures B.3 through B.6).

On June 11, 2002, acetate was also measured throughout the tank in addition to methane. Acetate was of interest because it can be produced by acetogenic bacteria and consumed by methanogenic bacteria. Only one sampling point yielded a detectable acetate concentration of greater than 50 mg/L (Figure B.4). A month later, the acetate pattern was similar, with only one sampling point having a detectable acetate concentration of between 10 and 50 mg/L. By the last sampling event on August 5, the distribution of acetate was more uniform. All sampling points had measurable acetate concentrations and all were less than 0.1 mg/L.

f. Quantification of Volatilization Losses

To quantify volatile losses of chlorinated constituents, ethene, ethane, and methane during the hydrogen sparge, samples of the ECRS tank headspace were taken within 30 minutes of the sparge on three separate dates. All three sampling events indicated that volatilization of PCE and reductive dechlorination daughter products were not a significant loss mechanism for reductive dechlorination daughter products as shown in Table 6. The amount of daughter products lost in the effluent as a percentage of the amount of PCE entering the ECRS tank ranged from 0.76 to 2.85%, with a mean of 2.17%. The percent volatilized was low due to the small volume of gas sparged and the relatively high groundwater velocity passing through the tank.

g. Hydrogen Distribution Trends Using Time Domain Reflectometry (TDR)

Hydrogen distribution and lifetime were monitored using TDR. TDR measures the % moisture content of the soil. By taking the difference in the TDR value before and after the sparge, the difference in the soil moisture can be determined. This value can be converted to a change in % gas saturation by dividing by the porosity of the aquifer matrix. Cross-sections in the X-Y and X-Z planes showing changes in % gas saturation can be found in Appendix C. Changes in gas saturation greater than 0.6% represent a value greater than background. Negative changes in % gas saturations indicate areas which experienced increases in % moisture due to the displacement of water by the injected gas.

Prior to bioaugmentation (February 18, 2002), TDR showed high gas saturations immediately after the sparge with gas saturations ranging from greater than 0.6 to greater than 5% (Figure C.1). TDR showed high concentrations of the gas at distances up to 3 feet away from the sparge point. Dissolved hydrogen may have extended beyond these points, but TDR measured only hydrogen in the gas phase.

Despite sparging the system in an identical manner (1 minute at 0.45 scfm), the hydrogen distribution in the ECRS tank changed by April 12, 2002 (Day 81), as shown in Figure C.2. The % gas saturation was lower and the radius of delivery was smaller.

The decreasing hydrogen trend continued throughout May and June (Figures C.3 and C.4), The decreasing hydrogen saturation did not impact the system performance in May as demonstrated by the absence or low concentrations of PCE, TCE, and cDCE throughout the tank on May 6 (Figure A.3). Sufficient hydrogen must have been delivered but was below the TDR resolution.

In July, large changes in % gas saturation were evident but only at one waveguide location (Figure C.5). The hydrogen gas injection volume was increased further to 1.59 standard cubic feet (scf) and the % gas saturation and distribution improved by August (Figure C.6). However, despite adding more than three times more gas, the hydrogen saturation and distribution were not as good as they were during the first few months of the experiment at the lower hydrogen injection volume of 0.45 scf.

Because TDR measurements were taken immediately after the hydrogen sparge, the difference in the percent gas saturation over time is unlikely to be due to increased hydrogen utilization by microbial populations, unless these populations were able to consume high levels of hydrogen in less than 13 minutes (the time required to take 46 waveguides measurements). It seems more likely that the formation of the sand pack changed over time (e.g., formation of microchannels) and this resulted in the differences in distribution.

h. Monitoring Data

The semi-weekly monitoring data can be found in Figure 16. The dissolved oxygen was generally less than 0.6 mg/L, indicating anaerobic conditions. The mean dissolved oxygen concentration for the entire experiment was 0.46 mg/L. ORP measurements were initiated later in the experiment but generally showed a similar pattern to the dissolved oxygen measurements. The ORP varied between 11.6 and -169.3 mV. These values were in the range where reductive dechlorination is expected to occur (USEPA, 1998). The pH stayed relatively constant with a mean pH value of 6.3 over the course of the experiment.

The temperature ranged from 13.4 to 30.1 ^{o}C, with a mean of 24.6 ^{o}C. It increased steadily because of the increasing ambient temperature throughout the summer in the facility where the experiments were being conducted. The Rice University culture is more effective at degrading PCE at temperatures near 22 ^{o}C than temperatures of 35 ^{o}C (Adamson et al., 2003). Therefore, part of the performance decline near the end of the test may be due to high temperatures.

i. Biodegradation Rate Constants

The Biochlor groundwater transport model was used to calculate biodegradation rate constants using centerline chlorinated solvent data from four separate sampling events spanning the six month experiment. Although these rate constants were estimated based on small data sets, they were nevertheless useful for comparing the relative biodegradation rates of the various chlorinated constituents and for qualitative comparison to reductive dechlorination rates under natural attenuation conditions.

As seen in Table 7, PCE was the constituent with the highest biodegradation rate constant, a trend typically observed in reductive dechlorination laboratory studies (Vogel and McCarty,1985). The biodegradation rate constants ranges were as follows:

Constituent	Rate Constant (1/yr)	Half-Life (days)
PCE	200-2000	0.13-1.3
TCE	70-200	1.3-3.6
cDCE	50-1000	0.25-5.0
VC	80-120	2.1-3.1

All the rate constants were 2-3 orders of magnitude greater than typical biodegradation rate constants estimated from field sites undergoing rapid biodegradation under reductive dechlorination under natural attenuation conditions (Aziz et al, 1999).

j. System Performance

The system performance was monitored over the course of the six-month experiment as summarized in Table 8. During the test, 82% of the total PCE entering the tank was removed, and 78% was removed by biotransformation. Fifty-three percent of the total chlorinated constituents were removed, with 46% being biodegraded. These performance data represent good removals, considering the effluent was located only 12 feet downgradient of the sparge well. Higher removal efficiencies would be expected at distances further downgradient due to other biodegradation processes such as anaerobic oxidation. Seventy-three percent mass balance closure was obtained using the chlorinated constituents and ethene concentrations in the influent, effluent, and off-gas and dividing by measured increases in chloride in the effluent.

Although there was a decline in performance due in part to carbon limitations and high temperatures, this is unlikely to be a factor in the field. At many sites there is a continuous background source of organic carbon and the mean groundwater temperatures are lower than those present in the latter half of the experiment.

As discussed in Section i, the biodegradation rate constants ranged from 200 to 2000 1/yr for PCE, 70 to 200 1/yr for TCE, 50 to 1000 for cDCE and 80 to 120 1/yr for vinyl chloride. These values are several orders of magnitude higher than rate constants measured at field sites undergoing rapid natural biodegradation. Therefore, the addition of hydrogen has the potential to increase biodegradation rates by several orders of magnitude over background levels, even at sites currently undergoing biodegradation.

Ample hydrogen was added to the system over the course of the experiment as shown in the table below. Only 1.7 moles of the 67.7 moles of hydrogen added, or 2.5%, could be accounted for by reductive dechlorination. It is likely that much of the hydrogen was used in acetogenic and methanogenic reactions. Despite the excess hydrogen present, methane concentrations remained below 2 mg/L and did not impact the removal efficiency of PCE.

Moles Hydrogen Added	Moles Hydrogen Used for Reductive Dechlorination	% Used for Reductive Dechlorination
67.7	1.7	2.5%

6.5.4 Conclusions

1. During the six-month experiment, good cumulative PCE removals (82%) were achieved over a short distance (18 ft) using only one sparge well. A mass balance closure of 73% was achieved.

2. Only 2% of the chlorinated constituents volatilized during sparing, indicating that volatilization was not a major loss mechanism for PCE or its reductive dechlorination products at the seepage velocity of 600 ft/yr employed in this experiment. Volatilization may be a bigger factor in aquifers with lower regional groundwater flow velocities.

3. Vinyl chloride did not accumulate to levels approaching the mean influent PCE concentration of 9.7 uM. Some vinyl chloride may have been lost via other degradation processes such as anaerobic oxidation.

4. Methanogenesis, sulfate reduction, and high hydrogen gas saturations did not prevent reductive dechlorination.

5. Reductive dechlorination rate constants using hydrogen biosparging were 2-3 orders of magnitude higher than those for field site undergoing rapid natural attenuation.

6. Hydrogen did not have adverse effect on the pH or water quality of the effluent, which can be a problem with liquid and semi-solid fermentation substrates.

7. The performance of the system declined during the experiment, either due to carbon limitation and/or high temperatures (>30 ^{o}C). These factors are unlikely to be a problem at most field sites.

6.6 Hydrogen Delivery Radius and Lifetime Study

6.6.1 Objectives

The objectives of this study were to determine the hydrogen delivery radius and lifetime under different injection conditions.

6.6.2 Methodology

For these experiments, a hydrogen/sulfur hexafluoride custom mixture (99.99% hydrogen and 0.01% sulfur hexafluoride (SF_6)) was used instead of pure hydrogen. SF_6 acted as a conservative tracer.

The hydrogen delivery radius was measured using three different measurements: dissolved hydrogen, dissolved SF_6 (a conservative tracer), and change in % gas saturation. Aqueous samples for dissolved hydrogen and SF_6 were taken from over 20 sampling locations within the tank using the same technique used for the collection of samples for chlorinated solvent analysis. Percent gas saturation was measured using TDR waveguides. TDR had a much lower resolution than the aqueous analyses, with a detection limit of 0.6% gas saturation in this system.

Hydrogen and SF_6 analyses were conducted at Rice University within 24 hours of sample collection. Hydrogen was measured using GC/TCD and SF_6 was analyzed using GC/ECD.

A key consideration in hydrogen biosparging is the fluidization pressure of the aquifer. Gas must be injected at pressures less than the fluidization pressure to avoid disruption of the aquifer matrix and channeling (USACE, 1997), which can reduce the hydrogen distribution and increase the amount of gas breakthrough to the vadose zone. For the ECRS system, the fluidization pressure of the 5.5 ft sand pack was calculated to be 4.4 psig. The injection flow rates used in these studies yielded injection pressures less than 3.2 psig. In Experiment 1, hydrogen was injected for 1 minute at 0.45 scfm and, in Experiment 2, hydrogen was sparged for 1 minute at 1.59 scfm. Higher flow rates were not possible due to the risk of fluidization.

6.6.3 Results

a. Hydrogen Delivery Radius

The extent of hydrogen delivery was determined by plotting hydrogen, SF_6, and TDR data in three planes as shown in the figures in Appendix D. SF_6 proved to be the best indicator for the delivery radius, due to its low detection limit relative to hydrogen. As seen in Figure C.1, SF_6 could be detected at 0-5 ug/L up to 7 feet away from the sparge point. There were some buoyancy effects with higher SF_6 concentrations located at higher points in the tank, but gas was dispersed greater than 4 feet radially 1 foot from the bottom of the tank.

Dissolved hydrogen measurements showed hydrogen present at distances up to 4 feet away from the sparge point, but the concentration distribution did not correspond well with the SF_6 measurements. Only four sampling locations yielded hydrogen concentrations greater than 1 ug/L, likely due to the higher detection limit of 1 ug/L for hydrogen relative to SF_6.

TDR measurements showed a smaller delivery radius than either SF_6 or hydrogen, because of its higher detection limit (0.6% gas saturation vs. 1 ug/L for hydrogen). TDR measurements showed very high gas saturations (>5%) within 1 foot of the sparge well.

In summary, SF_6 was the best indicator of hydrogen distribution and radius of influence because of its low detection limit. Sparging at 0.45 scfm for 1 minute yielded a maximum delivery radius of 7 ft.

In the field, the delivery radius is expected to be higher. First, it would be feasible to inject more gas under higher pressures given the higher fluidization pressure threshold due to the greater overburden depth. Second, the delivery radius would be greater because the sparge well would be deeper, which increases the time for the rising hydrogen gas to disperse. However, delivery radii in the field are not expected to exceed 10 ft (Cannata et al., 2000).

b. Hydrogen Lifetime Studies

Experiment 1

After the hydrogen sparge on March 24, 2002, the water in the tank was analyzed on March 24th, 25th, 26th, and 28th for hydrogen and the change in % gas saturation to determine how fast the hydrogen was being consumed by biological reactions. Hydrogen consumption can be attributed to a number of possible biological processes including methanogenesis, acetogenesis, iron reduction, and reductive dechlorination.

After 24 hours (Figure D.2), hydrogen was present at a concentration of greater than 25 ug/L at only one location 2 feet from the sparge point. TDR showed only two locations with gas saturations between >0.6 and 2%. Both were one foot from the sparge point. Hydrogen and TDR measurements showed the hydrogen distribution to shrink dramatically, while the SF_6 delivery radius shrank only from 7 ft to 5 ft.

After 48 hours (Figure D.3), hydrogen was present 2 ft from the sparge point and at 8 ft from the sparge point. TDR showed only one location with a gas saturation >0.6%. By the fourth day (Figure D.4), virtually all the hydrogen was gone, while high concentrations of SF_6 persisted. These results indicated that the hydrogen lifetime was about 4 days.

Between 2 and 4 days after the sparge, TDR showed that the % change in gas saturation was increasing. Because TDR is not specific for hydrogen, it is likely that the increased gas concentrations were due to other gases such as carbon dioxide or methane, both of which are produced through methanogenesis.

Experiment 2

In the second lifetime experiment, TDR was used to measure the hydrogen lifetime since dissolved hydrogen measurements had proved problematic in the first experiment and analytical problems in the laboratory precluded SF_6 measurements. Hydrogen was sparged for 1 minute at 1.59 scfm on August 6, 2002, four and a half months after the first hydrogen lifetime experiment. The TDR gas saturation maps can be found in Figures D.5 and D.6 in Appendix D.

Even though greater than three times more gas was added to the ECRS tank in this experiment versus Experiment 1, the gas delivery radius was smaller. This suggested that the nature of the sand pack had changed due to repeated sparging as discussed previously in Section 6.5.3g. After 24 hours, no gas saturation was evident. Therefore, even though more gas had been added in this experiment, the hydrogen lifetime was less than that observed in Experiment 1. This was most likely due to a higher biological demand for the injected hydrogen, as the bacterial populations (acetogens, methanogens, dechlorinators etc.) had four additional months to grow.

c. Hydrogen Losses to Headspace ("Vadose Zone")

In addition to delivery radius and lifetime studies, the amount of hydrogen lost to the headspace was also measured. The results for three different sampling events can be found in Table 9. When hydrogen was sparged at 0.45 scfm for 1 minute, only 1-2% of the hydrogen injected was lost to the headspace. Therefore, as much as 98-99% of the hydrogen injected was available for biological reactions, minimizing safety concerns regarding fugitive hydrogen.

Later, the ECRS tank was sparged with higher amounts of hydrogen (1.59 scfm for 1 minute) in an attempt to get better hydrogen distribution. Under this condition, 29.9% was lost to the headspace, leaving a maximum of 70.1% for biological reactions. The amount of hydrogen remaining for biological reaction was still significantly more than for the lower injection flow rate, but the percentage available for biological reactions had decreased.

6.6.4 Conclusions

1. The maximum dissolved hydrogen delivery radius when the hydrogen was sparged for a 1 minute at 0.45 scfm was seven feet as measured using SF_6. TDR yielded a smaller radius of 2 ft, because it indirectly measured % gas saturation.

2. Three weeks after bioaugmentation, the hydrogen persisted for 4 days (as determined by dissolved hydrogen) and 2 days (as determined by TDR) when sparged for 1 minute at 0.45 scfm. Four and a half months later, using more sparge gas (1 min at 1.59 scfm), the hydrogen lifetime was shorter (less than 24 hours using TDR), presumably due to a larger bacterial population.

3. At low injection flow rates of 0.45 scfm, only 1-2% of the injected gas was lost to the headspace. At the higher injection flow rate of 1.59 scfm, 30% of the injected gas was lost to the headspace.

4. Although the hydrogen delivery radius is a function of the aquifer matrix, sparging conditions, and depth of the sparge point, the hydrogen delivery radius is expected to increase with increasing depth of the sparge point in the field to a maximum of about 10 ft based on biosparging field studies.

6.7 Reductive Dechlorination of DNAPL Source

6.7.1 Objectives:

The objectives of this study were:

i) to determine the rate and extent of reductive dechlorination for an emplaced DNAPL source using low-volume pulsed hydrogen biosparging, and

ii) to determine if reductive dechlorination enhanced the source zone loss rate relative to abiotic DNAPL dissolution in the absence of reductive dechlorination.

6.7.2 Methodology

a. DNAPL Emplacement

One third of a liter of PCE DNAPL was pumped into each of the following three sampling lines (6,2,2.5), (6,5,2.5) and (8,3.5, 2.5) as shown in Figure 17. These locations were below the water table. The exact distribution of the DNAPL was unknown.

b. ECRS System Operation

The ECRS system was operated with recycle with a flow rate of 0.1 gpm. This corresponded to a hydraulic retention time of 11 days or a seepage velocity of approximately 600 ft/yr. Chlorinated constituents in the effluent were removed using granulated activated carbon prior to being circulated to the head of the tank. The influent was sampled periodically to ensure that the incoming water was treated to non-detect levels. Acetate was added in the influent to achieve a mean concentration of 13 mg/L to provide a source of carbon for the bacteria.

Eight weeks after DNAPL addition, 2 L each of Basal Salts Medium, and Trace Element Solutions I and II were added to the system because the water had been circulating for over 6 months and the effluent was found to be devoid of phosphate. The table below outlines the medium components in each of these solutions.

Basal Salts Medium	Trace Element Solution I	Trace Element Solution II
40 g/L KCl	50 mg/L $ZnCl_2$	1 g/L $(NaPO_3)_{16}$
40 g/L $MgCl_2$-$6H_2O$	50 mg/L $MnCl_2$-$4H_2O$	250 mg/L KI
40 g/L NH_4Cl	50 mg/L H_3BO_3	50 mg/L NH_4VO_3
14 g/L KH_2PO_4	250 mg/L $CoCl_2$-H_2O	
2.5 g/L $CaCl_2$-$2H_2O$	50 mg/L $NiCl_2$-$6H_2O$	
	50 mg/L Na MoO_4-$2H_2O$	

The ECRS tank was sparged daily, Monday through Friday. The sparging schedule was changed as the experiment progressed as shown in the table below. For the first 70 days, the

ECRS tank was sparged once daily for one minute through sparge point 1 at coordinates (6,3.5,0.5). The mean amount of hydrogen added per day was 0.5 scf. To encourage better hydrogen distribution throughout the entire tank, a manifold was constructed between 11/11/02 and 11/27/02 to allow the simultaneous sparging of sparge point 1 and sparge point 2 located at coordinates (12,3.5,0.5). During the manifold construction, sparge point 2 was sparged at 0.1 scfm. Thereafter, the system was sparged through both sparge points, first two times per day and then three times per day for the final 18 days of the experiment. The mean total amount of hydrogen added per day during the last two periods was 3.4 and 5.1 scf, respectively. Before, during and after the sparge, nitrogen was flushed through the tank headspace to remove chlorinated constituents and hydrogen. When sparging, the injection pressures were maintained in the 2 to 4 psig range to avoid fluidization of the sand pack.

Dates	**Days Since DNAPL Addition**	**Sparge Duration (min.)**	**Sparge Frequency (times/day)**	**Mean Total H_2 Added Per Day (scf)**		
				Pt. 1	**Pt. 2**	**Total**
8/23/02-11/11/02	0-70	1	1	0.5	0	0.5
11/12/02-11/26/02	71-95	1	1	0	0.1	0.1
11/27/02-1/23/03	96-153	1	2	1.1	2.3	3.4
1/24/03-2/11/03	154-172	1	3	1.8	3.3	5.1

c. Monitoring

Approximately twice weekly, the pH, dissolved oxygen, temperature, and ORP of the effluent were measured. Dissolved oxygen was measured using a YSI model 51B dissolved oxygen meter and probe, pH and temperature was determined using a 99/300 meter, and ORP was measured using an Orion Model 250A meter and probe. Dissolved oxygen, oxidation-reduction potential, and temperature were measured in-line using a flow-through cell.

One sample from the interior and effluent were generally taken twice weekly for VOC analysis. A sample from the influent was collected every 1-2 weeks. The sampling protocol is outlined in the next section.

d. VOC Sampling Protocol

Prior to taking water samples for analysis, 300 mL of water (approximately twice the line volume) was discarded. 50-mL glass serum bottles, previously preserved with 2 drops of concentrated sulfuric acid, were slowly filled to the 45 mL level with the aqueous sample and then immediately capped with a Teflon-lined septa and aluminum seal. The samples were put on ice or refrigerated until analysis. One sample from the interior and effluent were generally

taken twice weekly. Extensive sampling of the entire of the tank was performed six times over the course of the 6-month experiment.

Gas samples from the headspace were collected using summa canisters. With the nitrogen gas flowing and after the hydrogen sparge, the summa canister was connected to the off-gas line. The valve was opened and a grab sample of the headspace was collected in the canister.

e. Analytical Methods

The analytical methods used in this experiment were the same as those described in section 6.5.2 d.

6.7.3 Results

a. VOC Effluent Data

Within 7 days of DNAPL emplacement, PCE concentrations were detected in the effluent at concentrations greater than 20 uM as shown in Figure 18. The effluent PCE concentration increased until day 56 and then gradually decreased. PCE concentrations in the interior at coordinates (13, 3.5, 2.5) were much more variable, with one measurement on day 73 approaching the solubility of PCE (i.e., 864 uM or 143 mg/L).

TCE remained at low levels for the first 3 months of the experiment. After 84 days, the TCE levels began to rise shortly after sparging sparge point 2. Increased TCE concentrations corresponded to the addition of more hydrogen during the last half of the experiment.

Like TCE, cDCE was not produced in large amounts for the first three months. After 96 days and the addition of hydrogen through sparge point 2, the effluent cDCE concentration increased to concentrations in the 1-13 uM range. The cDCE concentration increased further to a maximum of 20 uM after day 154 when the mean volume of hydrogen added was increased from 3.4 to 5.1 scf/day.

The concentration trends for VC and ethene differed from PCE and TCE. VC concentrations were higher at the beginning of the experiment due to residual VC left over from the previous dissolved phase experiment. After 35 days, the VC concentration stabilized in the 0.3 to 0.5 uM range for the remainder of the experiment, despite increases in the volume of hydrogen added on days 96 and 154. Ethene concentrations remained low (< 0.07 uM) throughout the entire experiment.

Although a side issue, these data suggest that conventional wells (simulated by the effluent) can yield much different values than wells with smaller discrete sampling intervals (simulated by the interior sampling point). This data suggests that multilevel sampling systems may be warranted in close proximity to source areas.

The most complete picture of the VOC trends can be seen by analyzing the effluent composition as shown in Figure 18. During the first 20 days, the % PCE decreased while the %TCE increased as the result of decreasing PCE concentrations. Between days 31 and 84, the effluent composition remained remarkably constant with an average composition of 95 % PCE,

4 % TCE, and less than 1 % of cDCE, VC, and ethene. After day 84, the % PCE in the effluent began to decline as the second sparge point was brought on-line. Between days 84 and 154, the % PCE ranged from 50 to 85%. It was not until after day 157, that the % PCE declined dramatically to 12%. Increasing the amount of hydrogen added and allowing additional time permitted the PCE to be significantly degraded.

The %TCE showed complementary trends to the % PCE in the effluent. The percent TCE increased during the first 20 days and then remained constant at about 4 %. After day 84, the % TCE in the effluent increased and ranged from 13 to 41% for the remainder of the experiment. The % TCE did not increase significantly after day 157 as the % PCE declined, because of the production of cDCE from the TCE.

The % cDCE remained less than 4.2% for the first 94 days. Between days 94 and 161 after additional hydrogen was added, the % cDCE ranged between 5.6 and 26.2 %. After day 161 the % cDCE increased dramatically to 61%.

The %VC and % ethene were generally very low throughout the entire experiment. The % VC was high at the beginning of the experiment due to residual VC left over from the previous dissolved phase experiment. After 28 days, the % VC was less than 1.8% for the remainder of the experiment. Likewise, the % ethene remained at less than 1.7% for the duration of the experiment.

b. PCE Dissolution

A secondary objective of this experiment was to observe whether biodegradation would speed the rate of PCE dissolution. To evaluate this most accurately, it would have been necessary to have an abiotic control. This was not possible, however, since the DNAPL experiment directly followed the dissolved PCE experiment, which had involved the inoculation of the tank with a dechlorinating culture. However, in the DNAPL experiment, there was an extended period where very little PCE transformation occurred (i.e., between days 31 and 84). Therefore, this period of the experiment could approximate an abiotic control.

The slope of the plot of cumulative % of initial moles removed from the tank (that is the cumulative molar amount of chlorinated constituents leaving the tank divided by the total molar amount of PCE added to the tank initially) versus time gave an indication of whether the rate of dissolution increased when the transformation of PCE increased (Figure 19). As seen from the plot, the slope remained constant throughout the experiment indicating that the transformation of PCE to more soluble daughter products did not increase the rate of PCE dissolution from the DNAPL. Over the six month test, 45% of the emplaced DNAPL was removed from the tank.

c. Methane and Acetate

Methane and acetate were measured in the influent and effluent as shown in Figure 20.

Acetate was added to the influent to serve as a source of carbon for bacterial growth. The concentrations in the influent were variable but were generally in the 0-30 mg/L range, with a mean concentration of 13 mg/L. Effluent concentrations were generally lower indicating a net consumption of acetate.

Methane concentrations were also variable but generally increased over the course of the test. Higher methane concentrations were observed in the latter part of the experiment when the amount of hydrogen added to the system was increased. The rate of methanogenesis increased even though the extent of reductive dechlorination increased. As in the dissolved phase experiment, increased methane concentrations did not preclude the degradation of PCE.

d. VOC Data from Large Sampling Events

In addition to monitoring the influent and effluent semi-weekly for PCE and reductive dechlorination daughter products, six additional large sampling events were conducted over the course of the experiment. For these events, samples were collected from within the tank to characterize the chlorinated compound distribution. The concentration cross-sections for PCE through ethene for the X-Z vertical plane for all sampling events and the X-Y horizontal plane for the last 2 events can be found in Appendix E.

Figure E.1 presents the pre-DNAPL conditions. After DNAPL addition on August 23, 2002, a large sampling round was conducted on September 9, 2002 as shown in Figure E.2. Despite adding DNAPL at coordinates (8, 3.5,2.5), PCE concentrations near solubility were observed 6 feet downgradient of the DNAPL injection site at coordinate (14, 3.5,1), suggesting that free-phase PCE may have migrated downgradient. Low concentrations of TCE and c-DCE were observed 1.5 feet from the DNAPL injection site at coordinate (8, 3.5,1) suggesting that reductive dechlorination was possible in close proximity to a source.

By October 4 (day 42), elevated levels of cDCE were observed near the downgradient end of the tank (Figure E.3) compared to levels a month earlier (Figure E.2). VC and ethene levels were generally lower. A month later in November (day 73), the interior sampling points showed evidence of mostly PCE. By December, PCE concentrations had declined, while TCE and cDCE concentrations had increased in the downgradient portion of the ECRS tank. The increase in TCE and cDCE was likely due to the increased volume of hydrogen added to that area of the tank and /or additional time required for the growth of dechlorinating bacteria.

During the January 9 (day 139) sampling event, high concentrations of PCE (i.e. > 1000 uM or >166 mg/L) were present near the DNAPL addition points. In these high PCE concentration areas, there was limited production of TCE, non-detect levels of cDCE and very low levels of VC and ethene. Higher TCE and cDCE concentrations were evident a few feet downgradient from the high PCE concentration areas. Comparatively very little VC and ethene was generated. Similar trends were observed with the last sampling event on February 6, 2003 (day 167).

e. Methane and Acetate Data from Large Sampling Events

In addition to PCE and reductive dechlorination daughter products, methane and acetate were measured from multiple sampling points throughout the tank to map their respective distributions spatially and temporally. Methane and acetate distributions were of interest because methanogens and acetogens can compete with dechlorinating bacteria for hydrogen. In addition, high methane concentrations indicated regions that were sufficiently reduced and more conducive to reductive dechlorination. Data can be found in Appendix F.

Acetate was added to the ECRS as a source of carbon for the bacteria and did not serve as an electron donor for this culture (J. Hughes, personal communication). Until Jan. 9, 2003 (day 139), the acetate concentrations generally decreased. The last two sampling events showed

elevated acetate near sparge point 1 indicating that acetate was being produced by acetogens that consumed the additional hydrogen added to the system during the latter part of the experiment. Although acetate concentrations were elevated during the last two sampling events, sufficient hydrogen was present to also permit some reductive dechlorination and more reductive dechlorination was observed in the last two events compared to the earlier sampling events.

Methane concentrations generally increased over the course of the experiment, with maximum concentrations being observed during the Jan. 9, 2003 (Day 139) sampling event. Methane concentrations were generally higher at the downgradient end of the tank, with methane concentrations greater than 5 mg/L on the last day of the experiment. Despite these high methane concentrations, significant conversion of PCE to TCE and cDCE was nevertheless observed. Therefore, reductive dechlorination still occurred despite the consumption of hydrogen by the methanogens.

f. Quantification of Volatilization Losses

To quantify volatile losses of chlorinated constituents, ethene, ethane, and methane during the hydrogen sparge, samples of the ECRS tank headspace were taken within 30 minutes of the sparge on three separate dates. The amount of daughter products lost in the headspace as a percentage of the amount of PCE and daughter products leaving the ECRS tank effluent ranged from 0.05% to 2.0% as shown in Table 10. All three sampling events indicated that volatilization of PCE and reductive dechlorination daughter products was not a significant loss mechanism for reductive dechlorination daughter products at the groundwater flow velocity employed in this experiment.

The composition of chlorinated ethenes in the headspace was also indicative of the chlorinated composition of the effluent. At early times, PCE was the predominant constituent. By the end of the experiment, the composition had changed to include significant amounts of TCE and cDCE.

g. Monitoring Data

The monitoring data for the DNAPL experiment can be found in Figure 21. Throughout the entire experiment the dissolved oxygen concentration was below 1 mg/L. After 50 days, it was consistently less than 0.4 mg/L. Although the ORP was variable throughout the experiment, it was generally negative, and after 50 days it was consistently less than -100 mV, the redox potential range considered to be optimal for reductive dechlorination (Wiedemeier et al., 1999).

The temperature in the tank declined over the course of the experiment (from 30 ^{o}C to 15 ^{o}C), because the ambient temperature decreased. More transformation was observed near the end of the experiment when temperatures were lower. Unlike the temperature, the pH remained fairly constant, remaining between 6.5 and 7.5 throughout the experiment.

6.7.4 Discussion of DNAPL Experiment

a. Rate and Extent of Reductive Dechlorination in Source Zones

Unlike the dissolved phase experiment where significant reductive dechlorination occurred within the first few weeks of the experiment, significant reductive dechlorination of a simulated source zone took much longer. There are several possible reasons for this:

i. Insufficient residence time, due in part to the highly variable concentration distribution of PCE, may have been a factor. Shortly after DNAPL addition, PCE appeared to migrate to the downgradient end of the tank based on high PCE concentrations at locations four feet upgradient from the effluent (see section 6.7.3 c). The residence time for PCE dissolved from this location would be approximately 2 days. Because only sparge point 1 was receiving hydrogen at the beginning of the experiment, hydrogen may not have reached PCE in the downgradient portion of the tank and/or there was not sufficient residence time to observe the transformation.

ii. When hydrogen was added to the second sparge point after day 71, elevated levels of TCE and cDCE were observed, suggesting that insufficient electron donor was a more likely cause of the lack of reductive dechlorination at early times.

iii. Higher concentrations of PCE would require more bacteria to effect significant transformation. The lag time before transformation occurred may have been due to the time required for the bacterial population to grow to a sufficiently high density.

iv. The temperature may also have been a factor. The Rice University dechlorinating culture is more active at ambient temperatures near 22 ^{o}C (Adamson et al., 2003). As the ambient temperature declined from 30 ^{o}C at the beginning of the experiment, the extent of reductive dechlorination increased.

v. Higher concentrations of PCE may inhibit cDCE dechlorinating bacteria (Adamson et al., 2003).

The low production of VC and ethene is not due to the absence of bacteria that degrade cDCE and VC since VC was generated in the dissolved phase experiment. In addition, the slow transformation of PCE is unlikely due to competing methanogenic and acetogenic reactions as more reductive dechlorination occurred at the end of the experiment when methane and acetate concentrations were higher.

b. Effect of Reductive Dechlorination on Enhanced Dissolution.

A secondary objective of this work was to evaluate whether biological reductive dechlorination in a source area would speed the rate of PCE dissolution and decrease the source life time. It was expected that reductive dechlorination of PCE to more soluble daughter products would lead to increased dissolution of PCE from the DNAPL. However, the cumulative percent of chlorinated constituents exiting the tank did not increase at a faster rate as the experiment progressed (Fig. 19). The main explanation for why enhanced dissolution was not observed is that the groundwater flow rate was fast relative to the biodegradation rate, which was slow until the very end of this experiment. In other words, clean water was recharging the DNAPL source

zone faster than PCE was being transformed to TCE. Therefore reductive dechlorination did not serve to speed the rate of DNAPL dissolution in this experiment.

Another possible reason for why enhanced dissolution was not observed may be related to the small volume of neat PCE added to the tank. Even when no significant reductive dechlorination was occurring the mass of PCE leaving the ECRS system or rate of PCE dissolution declined. Therefore, any increased dissolution of the source affected by reductive dechlorination was off-set by declining PCE dissolution.

6.7.5 Conclusions

1. Some reductive dechlorination was observed within 1.5 ft of a DNAPL source.

2. Three to four months were required before significant reductive dechlorination (i.e., greater than 40% daughter products in the effluent) was observed. This may have been due to the lag time required for the bacteria to grow to sufficient numbers to effect significant transformation.

3. By the end of the six-month experiment, hydrogen addition was effective in transforming high PCE concentrations to yield an effluent with 12% PCE, 25% TCE, 65% cDCE, and 2% VC. Low levels of VC and ethene may have been due to short residence times or inhibition of cDCE dechlorinating bacteria by high levels of PCE and TCE.

4. Enhanced DNAPL dissolution was not observed in this experiment. This result was likely due to fast groundwater flow rates relative to biodegradation rates, but may also have been impacted by the small emplaced DNAPL source.

5. High temperatures may have hampered the performance of the system at the beginning of the experiment. Declining temperatures may have been a factor in the improved performance near the end of the experiment.

6. Methane concentrations greater than 3 mg/L did not preclude reductive dechlorination of PCE.

7.0 CONCLUSIONS

The purpose of this research was to investigate the efficacy of bioaugmentation and hydrogen biosparging for a simulated dissolved PCE plume and a PCE DNAPL source area. In addition, hydrogen gas delivery radius and persistence were examined under different conditions to shed light on suitable sparging conditions in the field. The following is a summary of the technical conclusions of this study, relevance to field applications, and a discussion of the economic feasibility of this technology.

BIOAUGMENTATION

To conduct the hydrogen biosparging experiments it was necessary to inoculate the experimental system with a dechlorinating culture. The simulated aquifer was inoculated with 30 gallons of a mixed dechlorinating culture from Rice University. In total, 4.3 grams of bacteria were added to the simulated aquifer.

Within 9 days, reductive dechlorination was observed. Furthermore, for 110 days the rate and extent of reductive dechlorination generally increased with time, suggesting bacterial growth. Bacterial activity was maintained over the one-year experimental period.

Relevance to Field Sites The rapid onset of dechlorination indicated that this culture may have utility as a culture to promote reductive dechlorination in field applications. This culture is also capable of complete reductive dechlorination to ethene.

HYDROGEN BIOSPARGING

Breakthrough Experiments

In this experiment**,** all flow rates and durations tested (i.e., <0.5 scfm) appeared to be safe for hydrogen operation, because of the low amount of gas added compared to the volume of gas in the headspace. In addition, the headspace was sparged with nitrogen to dilute any hydrogen that volatilized and to maintain an anaerobic environment during the biodegradation experiments. The maximum injection flow rate of 0.5 scfm and the associated injection pressure of 2.7 psig were constrained by the estimated fluidization pressure of 4.4 psig of the sand, including a safety factor of 40%.

Relevance to Field Sites. Prior to implementing a hydrogen sparging system, it is important to determine what injection pressure will cause fluidization and use a safety factor. Injection of gases at deeper intervals will permit high injection flow rates and gas volumes in the field.

An evaluation should be performed to determine whether an explosive environment could be generated if all the injected hydrogen off-gasses. This technology should not be implemented near sources of ignition.

Delivery Radius and Gas Persistence

The maximum dissolved hydrogen delivery radius when the hydrogen was sparged for a 1 minute at 0.45 scfm was seven feet as measured using SF_6. TDR yielded a smaller radius of 2 ft, because it indirectly measured percent gas saturation.

Three weeks after bioaugmentation, the hydrogen persisted for 4 days (as determined by dissolved hydrogen) and 2 days (as determined by TDR) when sparged for 1 minute at 0.45 scfm. Four and a half months later, using more sparge gas (1 min at 1.59 scfm), the hydrogen lifetime was shorter, presumably due to a larger bacterial population.

Relevance to Field Sites. Although the hydrogen delivery radius is a function of the aquifer matrix, sparging conditions, and depth of the sparge point, the hydrogen delivery radius is expected to increase with increasing depth of the sparge point in the field to a maximum of about 10 ft.

The persistence of hydrogen in a field application will be site-specific. This work indicated that sparging intervals between twice a week and once a day were effective for a simulated plume. As the bacterial populations grow, the hydrogen persistence is expected to decrease and the sparging frequency should be increased.

Effectiveness of Hydrogen Biosparging for Dissolved plumes

In this experiment, good PCE removals (82%) were achieved over a short distance (18 ft) using only one sparge well. A mass balance closure of 73% was achieved. Only 2% of the chlorinated constituents volatilized during sparing, indicating that volatilization was not a major loss mechanism for PCE or its reductive dechlorination products at the groundwater flow velocity (600 ft/yr) employed in this experiment. Vinyl chloride did not accumulate to levels approaching the mean influent PCE concentration of 9.7 uM. Some vinyl chloride may have been lost via other degradation processes such as anaerobic oxidation.

Methanogenesis, acetogenesis, sulfate reduction, and high hydrogen gas saturations did not prevent reductive dechlorination. Reductive dechlorination rate constants using hydrogen biosparging were 2-3 orders of magnitude higher than those determined for field sites undergoing rapid natural attenuation. However, only 2.5% of the added hydrogen was used for reductive dechlorination, indicating that other bacterial processes are a major sink for hydrogen.

***Relevance to field sites*:** Hydrogen biosparging should be effective in stimulating the reductive dechlorination of dissolved chlorinated solvents, providing dechlorinating bacteria are present and active at the site. Competing reactions such as methanogenesis, acetogenesis and sulfate reduction should not preclude reductive dechlorination but will act as significant sinks for hydrogen. Volatilization is not a significant loss mechanism at high groundwater flow velocities but may be a significant loss mechanism in aquifers with slow regional flow. Hydrogen should not have adverse effects on the pH or water quality of the effluent that can be a problem with some liquid and semi-solid fermentation substrates.

Effectiveness for Source Areas

This experiment demonstrated that some reductive dechlorination is possible within 1 to 2 feet of a PCE DNAPL source. Several months were required before significant reductive dechlorination was observed. This may have been due to the lag time required for the bacteria to grow to sufficient numbers to effect significant transformation, insufficient electron donor, and/or high temperatures. By the end of the six-month experiment, reductive dechlorination of PCE yielded an effluent composition of 12% PCE, 25% TCE, 61% cDCE and 2% VC. Low levels of VC and ethene may have been due to short residence times or inhibition of cDCE dechlorinating bacteria by high levels of PCE and TCE. Declining temperatures may have been a factor in the improved performance near the end of the experiment.

Enhanced DNAPL dissolution was not observed in this experiment. This result was likely due to fast groundwater flow rates relative to biodegradation rates, but may also have been impacted by the small emplaced DNAPL source and the short duration where vigorous biodegradation was observed.

Relevance to field sites. Biodegradation of solvent DNAPLS is possible using bioaugmentation and/or hydrogen biosparging. However, enhanced DNAPL dissolution may not be observed if the groundwater flow rate is significantly faster than the rate of reductive dechlorination.

ECONOMIC FEASIBILITY

Low-volume pulsed biosparging is best suited for sites where large quantities of donor need to be injected, and where direct-push wells can be used.

The attractiveness of hydrogen as an electron donor is its low cost. The cost for industrial grade hydrogen gas is approximately $0.11 per SCF delivered to a site, or about $0.09 per mole of hydrogen.

The most significant capital cost for system implementation is the installation of the sparge wells. Installation costs can be minimized if direct push wells at $500 to $1,000 per well can be used. Simple delivery skids can be constructed for under $20,000. Injection well spacing of 10 ft should be used for design purposes. Installation of a permeable reactive wall of hydrogen sparge wells may be the most economical configuration at some sites.

A planning-level budget for a 100 ft by 100 ft treatment zone down to 30 ft was developed as shown below. Hydrogen injection wells on 10 ft. centers installed using a direct-push rig was assumed for this generic design.

Cost of Low-Volume Pulsed Biosparging
For 100 Ft by 100 Ft Treatment Zone

Element	Cost ($)
Capital Cost	
Planning and Preparation	$30,000
Mobilization/Demobilization/Per Diem	$5,000
Site Labor (assume 30 days for well installation @ $75/hr, 5 days for startup)	$25,000
Equipment and Appurtenances - Injection Points (assume $2500/day, 4 wells/day, 121 injection wells) - Process Skid + Shipping - Wellhead Equipment ($100/well) - Manifolds (assume 800 ft 1" PVC @ $5/ft for labor+materials plus $7K fittings)	$76,000 $15,000 $12,000 $11,000
Baseline Laboratory Analyses (assume 6 existing monitoring wells)	$3,000
Reporting	$20,000
Total Capital Costs	**$197,000**
Annual Operating Costs	
Direct Labor (Process Monitoring) (assume 1 hr per week by on-site technician)	$2,000
Project Management (assume 2 hrs/month @ $80/hr)	$2,000
Hydrogen (assume $30 per 260 ft^3 cylinder) (assumes 2 sparges/week of 50 scf)	$70,000
Sampling Labor (four events @ 2 days/event) (assume on-site personnel, 2-person team @100/hr combined for both people)	$8,000
Sampling Equipment and Supplies	$4,000
Laboratory Analysis	$12,000
Reporting	$12,000
Annual Operating Costs	**$110,000**

8.0 TRANSITION PLAN AND RECOMMENDATIONS

Hydrogen biosparging is a simple technology that is easy to implement. Its configuration can be tailored to site-specific requirements, making it very flexible. For example, sparge points can be installed to act as a passive barrier to plume migration or a larger array of sparging wells can be installed for active plume remediation or source zone remediation.

Although this study focused on the use of hydrogen biosparging for treating chlorinated solvent plumes and source areas, hydrogen biosparging can be used for a host of different contaminants, including perchlorate, 1,1,1-trichloroethane, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX).

Because chlorinated solvent contamination is frequently encountered at military installations, and there are many DoD sites across the country, the implementation of hydrogen biosparging at military sites represents an effective method to transition this technology to widespread use.

Currently direct hydrogen delivery is a patented technology (Hughes, Newell, and Fisher - U.S. Patent 5,602,296, February 11, 1997). Under contract F41624-97-8020, the Air Force has funded the initial development of hydrogen delivery technology. The entire DoD has a royalty-free license from Groundwater Services to use both hydrogen biosparging and dissolved hydrogen delivery, which will facilitate the use of this technology on military installations. Furthermore, as part of AFCEE contract F41624-97-8020, guidance documents will be written that outline how to build and operate these systems.

Currently pilot test projects have been implemented at the following sites:

Site	Facility	Description	Duration	Status
Launch Complex 15	Cape Canaveral, FL	Low-volume pulsed hydrogen biosparging in 3 vertical wells	18-month test	Project completed
OJET Site	Offutt AFB, NE	Dissolved hydrogen recirculation system	15-month test	Project on-going
Site 17	Beale AFB, CA	Low-volume pulsed hydrogen biosparging in 2 vertical wells in a fine-grained unit.	12-month test	Project on-going
PSC-3 Site	Marines Corps Logistics Facility, Albany, GA	High-pressure pneumatic sparging with hydrogen	6-month test	Project completed
Site 73	Camp Lejeune, NC	Low-volume pulsed hydrogen biosparging in 900 ft horizontal well	9-month test	Project on-going

Future transition work will include:

- Writing conference proceedings papers and journal articles;
- Writing a case study in the AFCEE Bioremediation Principals and Practices Manual;
- Encouraging applications in private sector.

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GSI Job No. G-2535
Issued: October 7, 2003

GROUNDWATER
SERVICES, INC.

FINAL REPORT FOR LOW-VOLUME PULSED BIOSPARGING OF HYDROGEN FOR BIOREMEDIATION OF CHLORINATED SOLVENT PLUMES

Groundwater Services, Inc., Houston, TX

TABLES

GROUNDWATER SERVICES, INC.

TABLE 1
CHARACTERISTICS OF SAND USED IN ECRS TANK

Low Volume Pulsed Hydrogen Biosparging Final Report
SERDP, Arlington, VA

Parameter	Value
Texture	Silty Fine Sand
Hydraulic Conductivity	0.1 cm/s
pH	6.2
foc	0.0012
porosity[1]	0.35

Notes:
1. Porosity estimated from baseline TDR measurements.
2. The hydraulic conductivity was determined using ASTM Method D2434.

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SERVICES, INC.

TABLE 2
HELIUM BREAKTHROUGH EXPERIMENT DATA

Low Volume Pulsed Hydrogen Biosparging Final Report
SERDP, Arlington, VA

Flow Rate (scfm)	Time (min.)	He Volume Added (ft^3)	Headspace Helium Conc.[1.] % (v/v)	Pressure at Sparge Pt. (psig)	Max. Breakthrough Radius[2.] (ft)
0.01	17	0.17	0.13	2.5	2.0
0.03	7.5	0.23	0.18	2.6	2.5
0.064	4.3	0.28	0.22	2.6	2.5
0.12	4.3	0.52	0.41	2.5	2.5
0.18	3.9	0.71	0.56	2.5	2.5
0.27	3.8	0.99	0.79	2.6	2.5
0.53	2.3	1.24	0.98	2.7	2.8

NOTES

1. The headspace helium concentration was calculated assuming 100% of the helium off-gassed and a well-mixed headspace.
2. The maximum breakthrough radius was determined from photographs of the gas breakthrough.

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TABLE 3
HELIUM DELIVERY RADIUS

Low Volume Pulsed Hydrogen Biosparging Final Report
SERDP, Arlington, VA

Flow Rate (scfm)	Time (min.)	He Volume Added (ft^3)	Max. Delivery Radius[1.] (ft)
0.06	2.0	0.13	3.3
0.12	2.0	0.24	4.3
0.27	1.0	0.27	4.0
0.53	1.0	0.53	3.5
0.53	0.5	0.27	4.0

NOTES

1. The maximum delivery radius was determined at the centerline of the tank using TDR output. The delivery radius was delineated at 0.05% change in soil moisture.

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TABLE 4
LABORATORY ANALYTICAL METHODS FOR BIOSPARGING EXPERIMENTS

Low Volume Pulsed Hydrogen Biosparging Final Report
SERDP, Arlington, VA

Analytical Parameter	Method	Sample Volume	Sample Preservation
Volatile Organics [1]	GC/FID	45 mL	<pH 2, H_2SO_4
Chloride	4500- Cl^- B	45 mL	<pH 2, H_2SO_4
Ethene	GC/FID	45 mL	<pH 2, H_2SO_4
Hydrogen	GC/TCD	45 mL	<pH 2, H_2SO_4
Methane	GC/FID	45 mL	<pH 2, H_2SO_4
SF6	GC/ECD	45 mL	<pH 2, H_2SO_4
Acetate	GC/FID	45 mL	<pH 2, H_2SO_4

Notes:

1. Volatile organic analytes include: PCE, TCE, cis-1,2-DCE, and vinyl chloride.
2. Analyses were conducted at Rice University.
3. All analytes, with the exception of chloride, were analyzed from the same sampling container.

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TABLE 5
BIOCHLOR INPUT PARAMETERS

Low Volume Pulsed Hydrogen Biosparging Final Report
SERDP, Arlington, VA

Parameter	Value
$V_{s\ 3/24/02}$	710.8 ft/yr
$V_{s\ 5/6/02}$	500.6 ft/yr
$V_{s\ 7/11/02}$	474.3 ft/yr
$V_{s\ 8/5/02}$	482.5 ft/yr
n_e	0.35
α_x	0.5 ft
ρ	1.6 kg/L
f_{oc}	0.0012
$K_{oc\ PCE}$	426 L/kg
$K_{oc\ TCE}$	130 L/kg
$K_{oc\ cDCE}$	125 L/kg
$K_{oc\ VC}$	30 L/kg
Mean R	1.97
Source Thickness	4.9 ft
Width	7 ft
C_o	1.6 mg/L

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TABLE 6
RESULTS OF VOLATILIZATION STUDIES - Dissolved Phase Study
Volatile Organic Compounds

Low Volume Pulsed Hydrogen Biosparging Final Report
SERDP, Arlington, VA

DATE	CONSTITUENT	HEADSPACE CONC. (ug/m3)	MMOLES/DAY LEAVING TANK	% OF PCE ENTERING TANK
3/23/2002	cis-1,2-dichloroethene	<4330	--	--
	Ethene	<2679	--	--
	Trichloroethene	<5871	--	--
	Tetrachloroethene (PCE)	<7411	--	--
	Vinyl Chloride	6696	0.1	2.85
	TOTAL			**2.85**
5/5/2002	cis-1,2-dichloroethene	864	0.009	0.04
	Ethane	2679	0.086	0.44
	Ethene	<2679	--	--
	Methane	48571	NA	--
	Trichloroethene	1022	0.007	0.04
	Tetrachloroethene (PCE)	1364	0.008	0.04
	Vinyl Chloride	2666	0.041	0.21
	TOTAL			**0.76**
7/10/2002	cis-1,2-dichloroethene	<672	--	--
	Ethane	<2679	--	--
	Ethene	<2679	--	--
	Methane	7000	NA	--
	Trichloroethene	4590	0.033	0.85
	Tetrachloroethene (PCE)	13995	0.081	2.06
	Vinyl Chloride	<437	--	--
	TOTAL			2.91
			MEAN :	**2.17**

Notes:
1. Samples analyzed by Research Triangle Park Laboratories, Inc., Raleigh, N.C.
2. < = Compound analyzed for but not detected at the detection limit specified. NA= Not applicable
3. On 3/24/02, all constituents were analyzed using EPA Modified Method 18 GC/FID. On subsequent dates, the VOCs were analyzed using Method TO-14A GC/MS and methane, ethene, and ethane were analyzed using EPA Modified Method 18 GC/FID.
4. The mmoles/day leaving the tank is based on the concentration in the headspace times the 4.2 gpm (nitrogen purge flow rate) for 60 minutes/day.
5. % of PCE Entering Tank was calculated by dividing the mmole/day of VOC leaving the tank in the off-gas and dividing it by the mean mmoles/day. of PCE entering the tank in the 20 days prior to the sampling date.
6. During all three events, hydrogen was sparged for 1 min at 0.45 scfm.

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TABLE 7
BIODEGRADATION RATE CONSTANTS

Low Volume Pulsed Hydrogen Biosparging Final Report
SERDP, Arlington, VA

	Biodegradation Rate Constants (1/yr)				
Consituent	**3/23/2002**	**5/5/2002**	**7/10/2002**	**8/4/2002**	**Mean**
PCE	2000	NC	200	250	817
TCE	NC	NC	70	200	135
cDCE	90	NC	50	1000	380
VC	120	120	120	80	110

Notes:
1. Biodegradation rate constants found by qualitatively finding a best fit line to experimental data using BIOCHLOR Version 2.2.
2. NC indicates that there was not enough data to calculate a rate constant.

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TABLE 8
ECRS PERFORMANCE - Dissolved Phase Study
Low Volume Pulsed Hydrogen Biosparging Final Report
SERDP, Arlington, VA

Constituent	Moles In	Moles Out (Water)	% Removed	Moles Out (Off-Gas)	Moles Sorbed	% in Off-Gas	% Sorbed	% Biotransformed
PCE	0.776	0.139	82.1	0.003	0.027	0.6	3.4	78.3
TCE	0.000	0.051	-6.6	0.002	0.012	0.3	1.5	-8.3
cDCE	0.000	0.076	-9.8	0.000	0.000	0.06	0.0	-9.9
VC	0.000	0.102	-13.1	0.006	0.001	0.9	0.1	-14.0
Ethene	0.000	0.007	-0.9	0.003	0.000	0.6	0.0	-1.4
Total Chlorinated	0.776	0.368	52.6	0.011	0.040			46.2
							Unaccounted Ethenes	**% Other Reactions**
Total Ethenes	0.776	0.375		0.014	0.040		0.35	44.7
								% Closure
Chlorine	3.1	0.963		0.025	0.143			72.6

Notes:
1. The % PCE Removed was calculated by subtracting the total moles of PCE that left the tank in the effluent from the total PCE moles entering the tank over the course of the experiment and dividing by the total PCE moles entering. The % Total Chlorinated Removed was calculated in a similar fashion. Negative % removed values represent the % produced.
2. The % PCE Biodegraded was calculated by subtracting the total moles of PCE that left the tank in the effluent and offgas and the total moles of PCE sorbed to the aquifer matrix (assuming equilibrium) from the total PCE moles entering the tank over the course of the experiment and dividing by the total PCE moles entering. The % Total Chlorinated Biodegraded was calculated in a similar fashion.
3. The moles sorbed was estimated based on the average concentration of each of the constituents in the tank during the last sampling period and assuming equilibrium between the sand and the water.
4. % Other Reactions was calculated by taking the number of moles of unaccounted for ethenes and dividing by the number of moles of PCE entering the tank times 100%.
5. % Closure was calculated by taking the change in chlorine and dividing by the increase in measured chloride of 2.7 moles.

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TABLE 9
RESULTS OF HYDROGEN BREAKTHROUGH STUDIES

Low Volume Pulsed Hydrogen Biosparging Final Report
SERDP, Arlington, VA

DATE	Temperature (^{o}C)	H_2 ADDED (scf)	H_2 ADDED AT AMBIENT TEMP. (ft^3)	H_2 LOST TO HEADSPACE (ft^3)	% H_2 LOST
6/6/2002	28	0.45	0.5	0.009	1.8
7/9/2002	29	0.45	0.5	0.006	1.2
8/22/2002	30	1.59	1.76	0.528	29.9

Notes:
1. Hydrogen was measured using a CEA Instruments Series U hydrogen meter and probe. The detection limit is approximately 50 ppm.
2. The hydrogen added was determined by taking the flow rate times the sparge length (1 minute in all cases).
3. To determine the total volume of hydrogen that left the tank in the headspace, a graph of hydrogen concentration over time was generated and the area below the curve was calculated using the gas flow rate leaving the tank.

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TABLE 10
RESULTS OF VOLATILIZATION STUDIES - DNAPL Experiment
Volatile Organic Compounds

Low Volume Pulsed Hydrogen Biosparging Final Report
SERDP, Arlington, VA

DATE	CONSTITUENT	HEADSPACE CONC. (ug/m3)	µMOLES/DAY LEAVING TANK	% of PCE + Daughters LEAVING TANK
10/4/2002	cis-1,2-dichloroethene	1.7	0.009	0.000
	Ethane	<1339	--	0.000
	Ethene	<1250	--	0.000
	Trichloroethene	24.1	0.088	0.005
	Tetrachloroethene (PCE)	247.5	0.715	0.037
	Vinyl Chloride	9.5	0.073	0.004
	TOTAL	**282.8**	**0.885**	**0.046**
12/4/2002	cis-1,2-dichloroethene	67.1	0.687	0.007
	Ethane	<1339	--	0.000
	Ethene	<1250	--	0.000
	Trichloroethene	779	7.973	0.079
	Tetrachloroethene (PCE)	1932.7	19.781	0.197
	Vinyl Chloride	20.4	0.208	0.002
	TOTAL	**2799.2**	**28.649**	**0.285**
2/6/2002	cis-1,2-dichloroethene	1149.2	17.644	0.279
	Ethane	<1339	--	0.000
	Ethene	<1250	--	0.000
	Trichloroethene	9067.2	139.206	0.894
	Tetrachloroethene (PCE)	7638.5	117.271	0.753
	Vinyl Chloride	373	5.726	0.037
	TOTAL	**18227.9**	**279.847**	**1.963**

Notes:
1. Samples analyzed by Research Triangle Park Laboratories, Inc., Raleigh, N.C.
2. < = Compound analyzed for but not detected at the detection limit specified. NA= Not applicable
3. VOCs were analyzed using Method TO-14A GC/MS and methane, ethene, and ethane were analyzed using EPA Modified Method 18 GC/FID.
4. The umoles/day leaving the tank is based on the concentration in the headspace times the 4.2 gpm (nitrogen purge flow rate) for the first, second, and third event of 30 minutes/day, 40 minutes/day, and 60 minutes/day, respectively.
5. % of PCE +Daughters leaving tank was calculated by dividing the umole/day of VOC leaving the tank in the off-gas by the mean umoles/day of total chlorinated ethenes leaving the tank.
6. During all the first event, hydrogen was sparged once per day at 1.2 scfm for 1 minute. During the second event, hydrogen was sparged twice per day through two different sparge points at a total hydrogen flow of 0.6 scfm. During the third event hydrogen was sparged three times per day through 2 sparge points at a total hydrogen flow per sparge event of 1.9 scfm.

GSI Job No. G-2535
Issued: October 7, 2003

GROUNDWATER
SERVICES, INC.

FINAL REPORT FOR LOW-VOLUME PULSED BIOSPARGING OF HYDROGEN FOR BIOREMEDIATION OF CHLORINATED SOLVENT PLUMES

Groundwater Services, Inc., Houston, TX

FIGURES

GSI Job No. G-2535
Issued: October 7, 2003

GROUNDWATER
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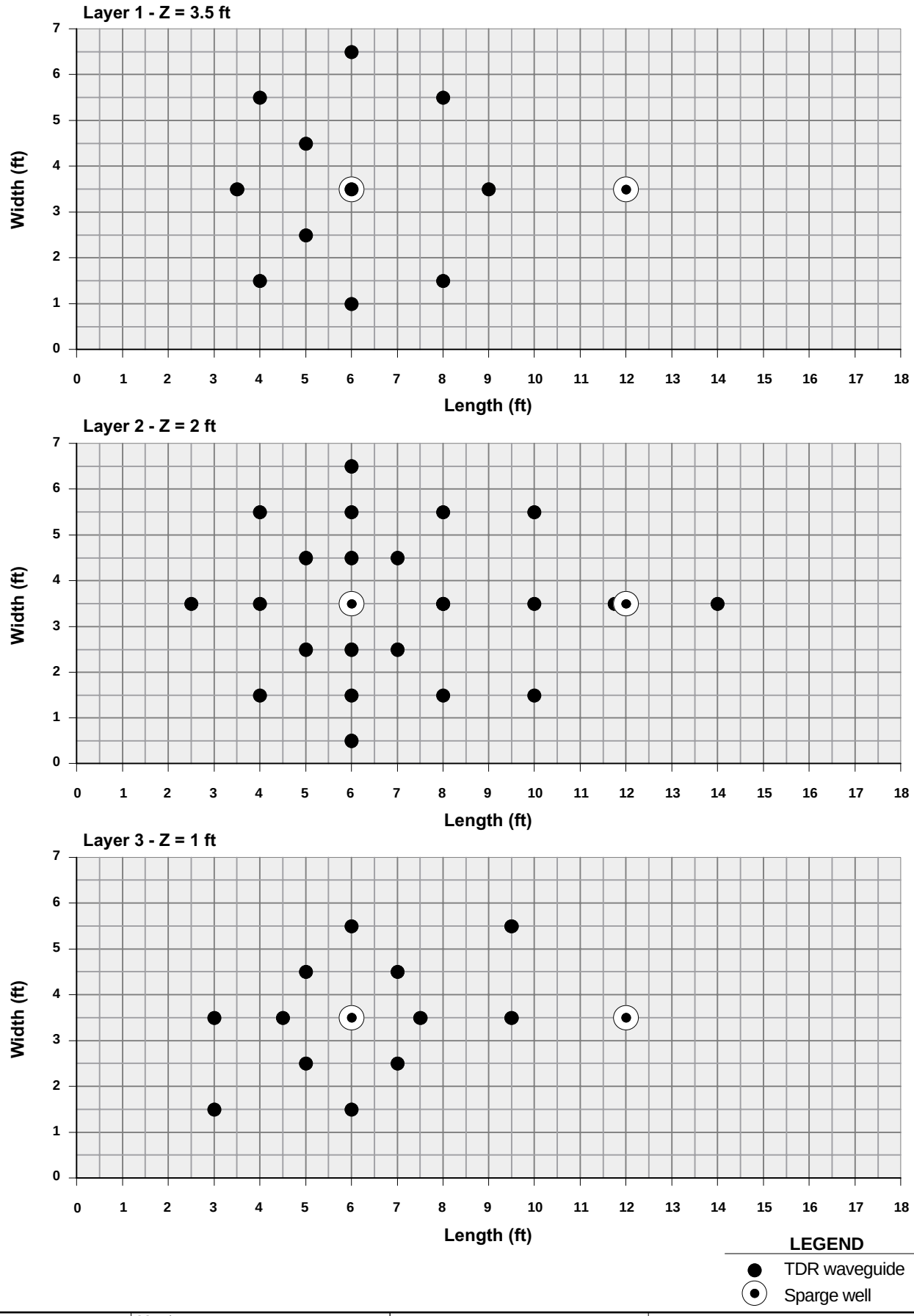
FINAL REPORT FOR LOW-VOLUME PULSED BIOSPARGING OF HYDROGEN FOR BIOREMEDIATION OF CHLORINATED SOLVENT PLUMES

Groundwater Services, Inc., Houston, TX

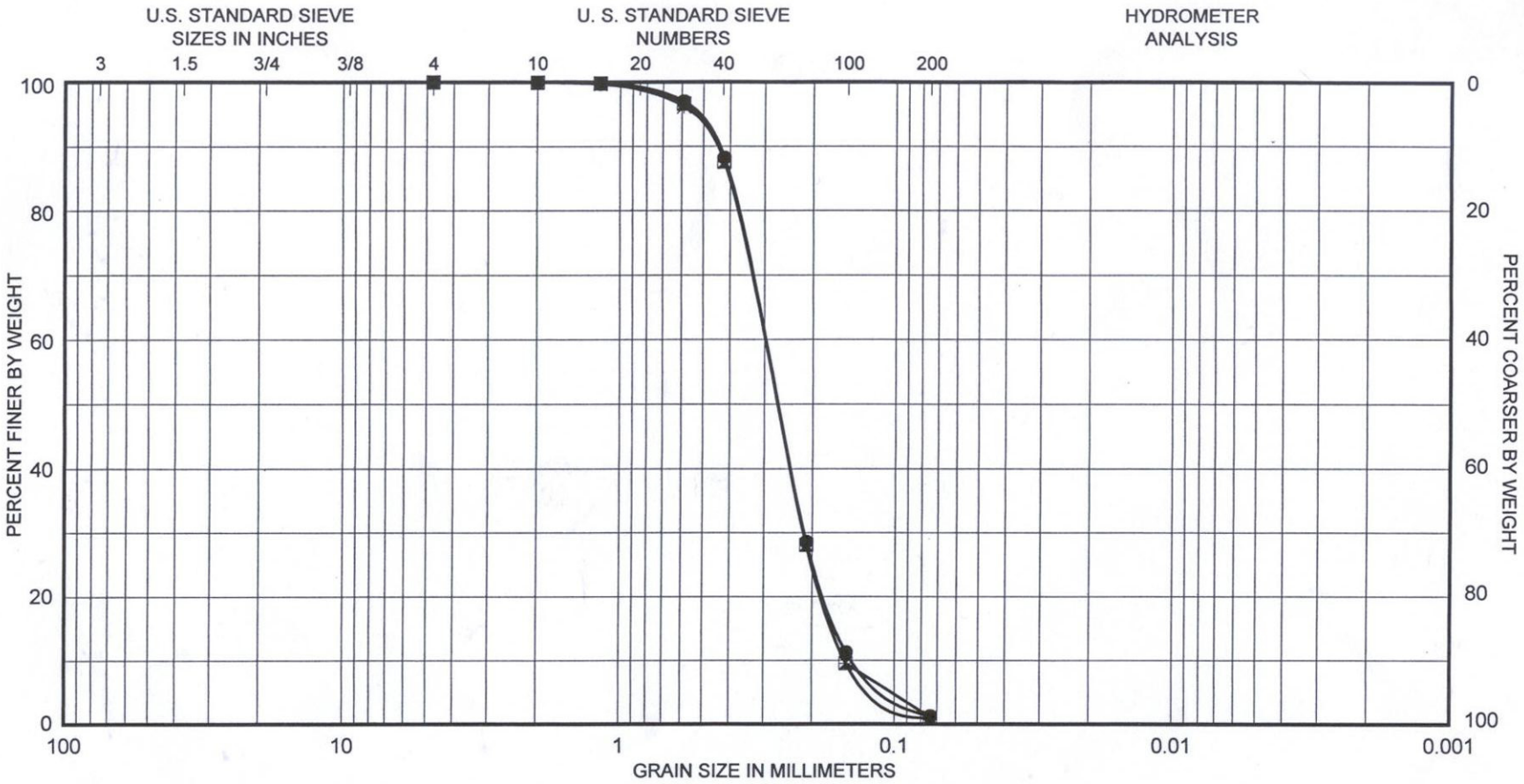
FIGURES (cont'd)



GROUNDWATER SERVICES, INC.

GSI Job No.	G-2535-107	Drawn By:	CCJ
Issued:	7/16/03	Chk'd By:	CEA
Revised:	_____	Aprv'd By:	
Scale:	As Shown	**FIGURE 1**	

PLAN VIEW OF TDR WAVEGUIDE LOCATIONS



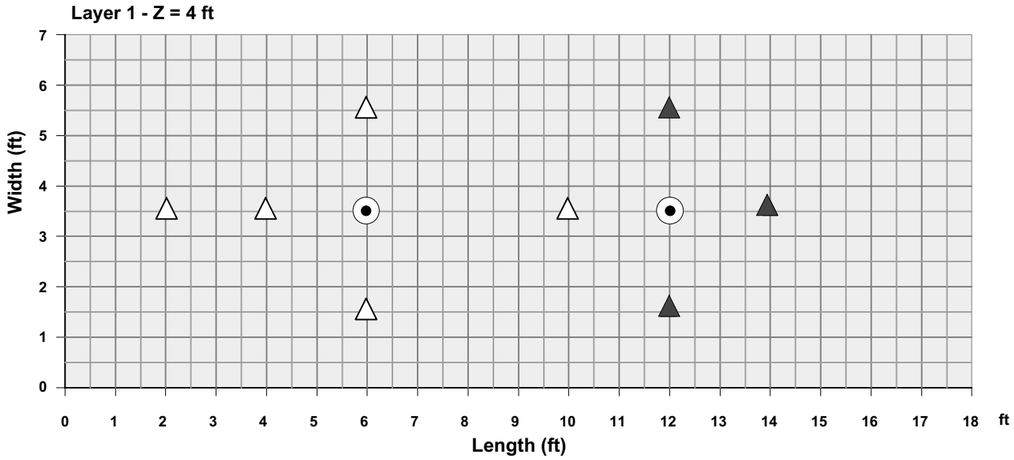
GRAVEL		SAND			SILT or CLAY
Coarse	Fine	Coarse	Medium	Fine	

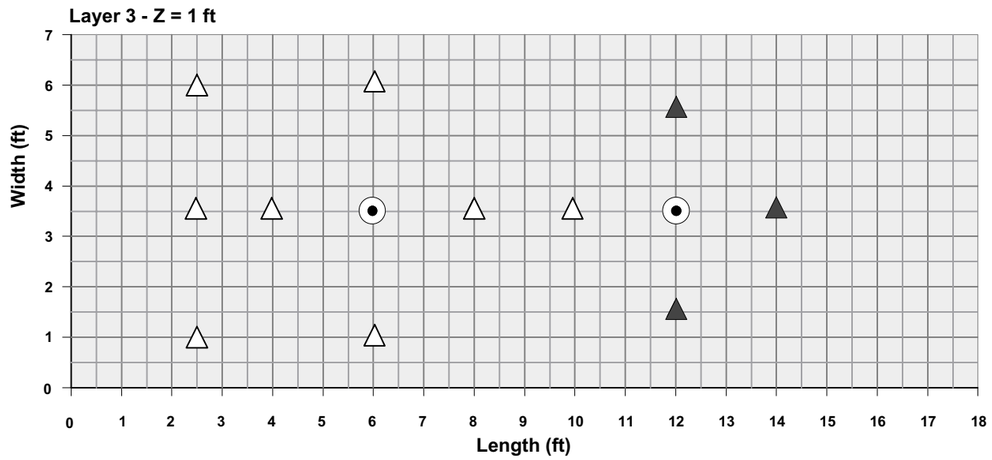
SYMBOL	BORING	DEPTH, FT.	CLASSIFICATION
●	Sand-01	0.1	Silty Sand, light brown
⊠	Sand-02	0.0	Silty Sand, light brown
✳	Sand-03	0.0	Silty Sand, light brown

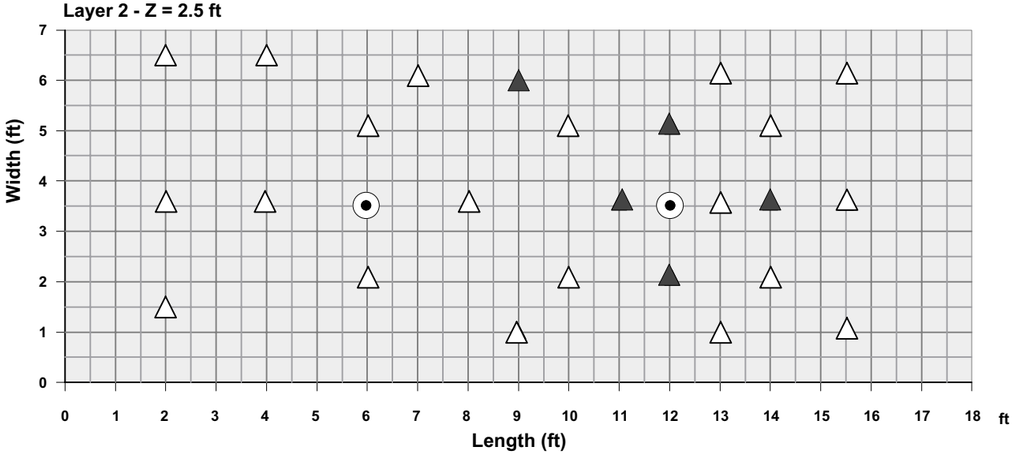
GROUNDWATER SERVICES, INC.

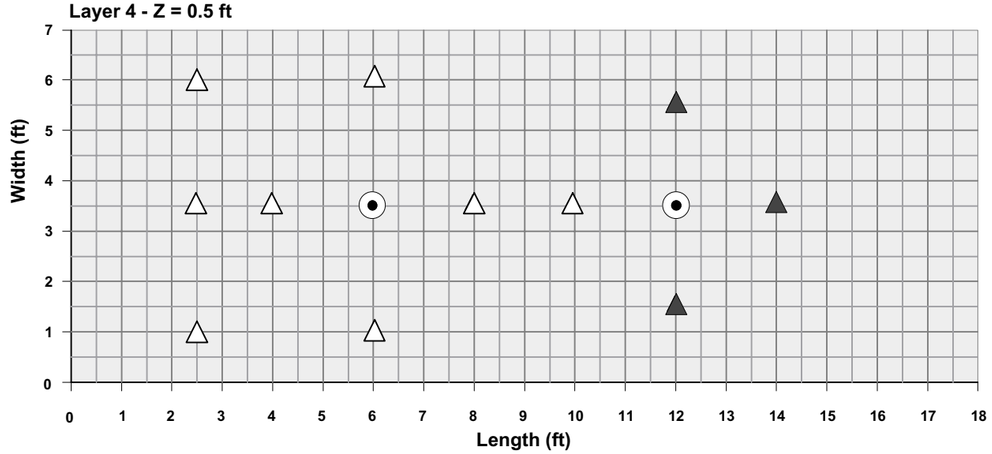
GSI Job No.	G-2535-107	Drawn By:	CCJ
Issued:	7/16/03	Chk'd By:	CEA
Revised:	_____	Aprv'd By:	
Scale:	As Shown	**FIGURE 2**	

ECRS SAND GRAIN SIZE DISTRIBUTION









LEGEND

- Sparge well
- Back-up sampling locations
- Sampling locations

GROUNDWATER SERVICES, INC.

GSI Job No.	G-2535-107	Drawn By:	CCJ
Issued:	7/16/03	Chk'd By:	CEA
Scale:	As Shown	Aprv'd By:	

PLAN VIEW OF SAMPLING LOCATIONS IN ECRS TANK

FIGURE 3

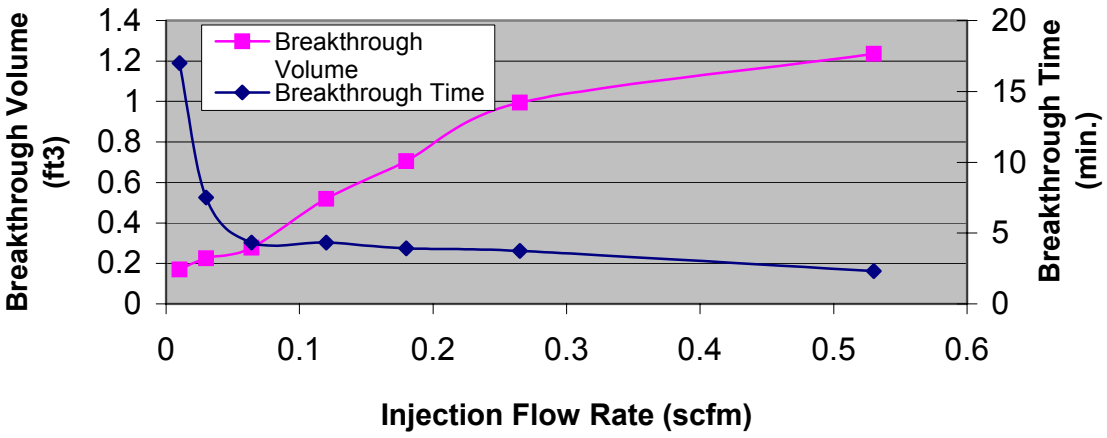


Figure 4. Breakthrough Volume and Time vs. Injection Flow Rate

Figure 5. Typical Breakthrough Pattern

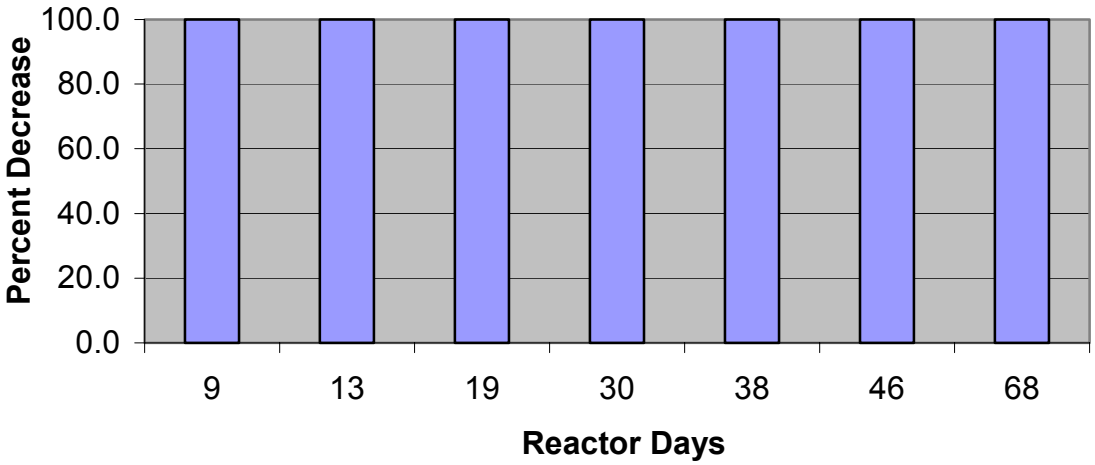


Figure 6. Percent Decrease in PCE Mass After 24 hours in Bioreactor Microcosms

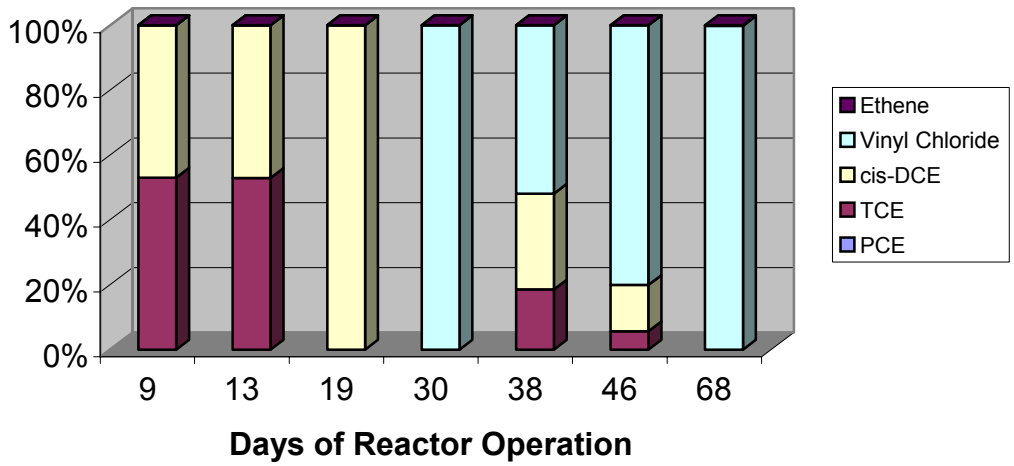
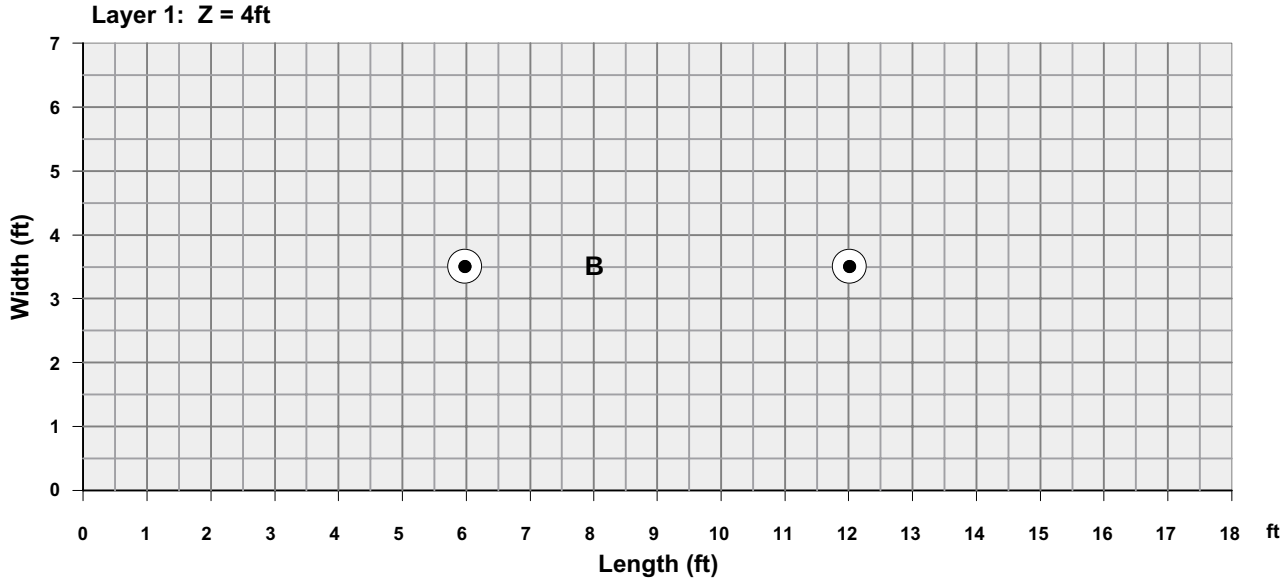
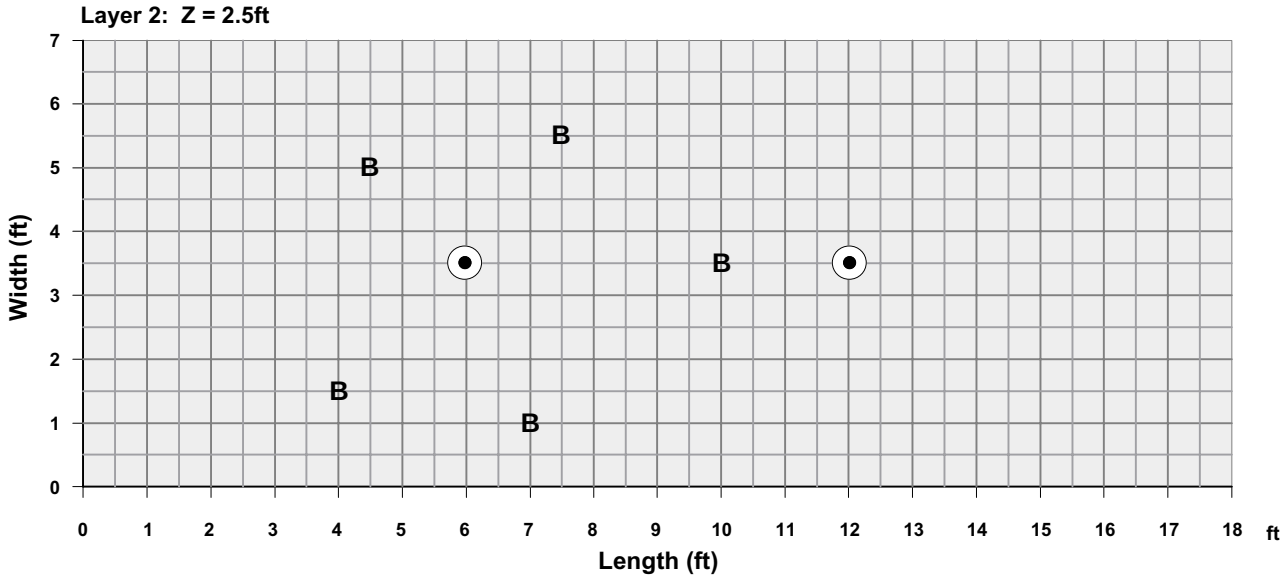


Figure 7. Percentages of Gases Recovered from Bioreactor Microcosms





LEGEND

⊙	Sparge well
B	Bacterial addition points

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Scale:	As Shown	**FIGURE 8**	

BIOAUGMENTATION LOCATIONS IN ECRS TANK

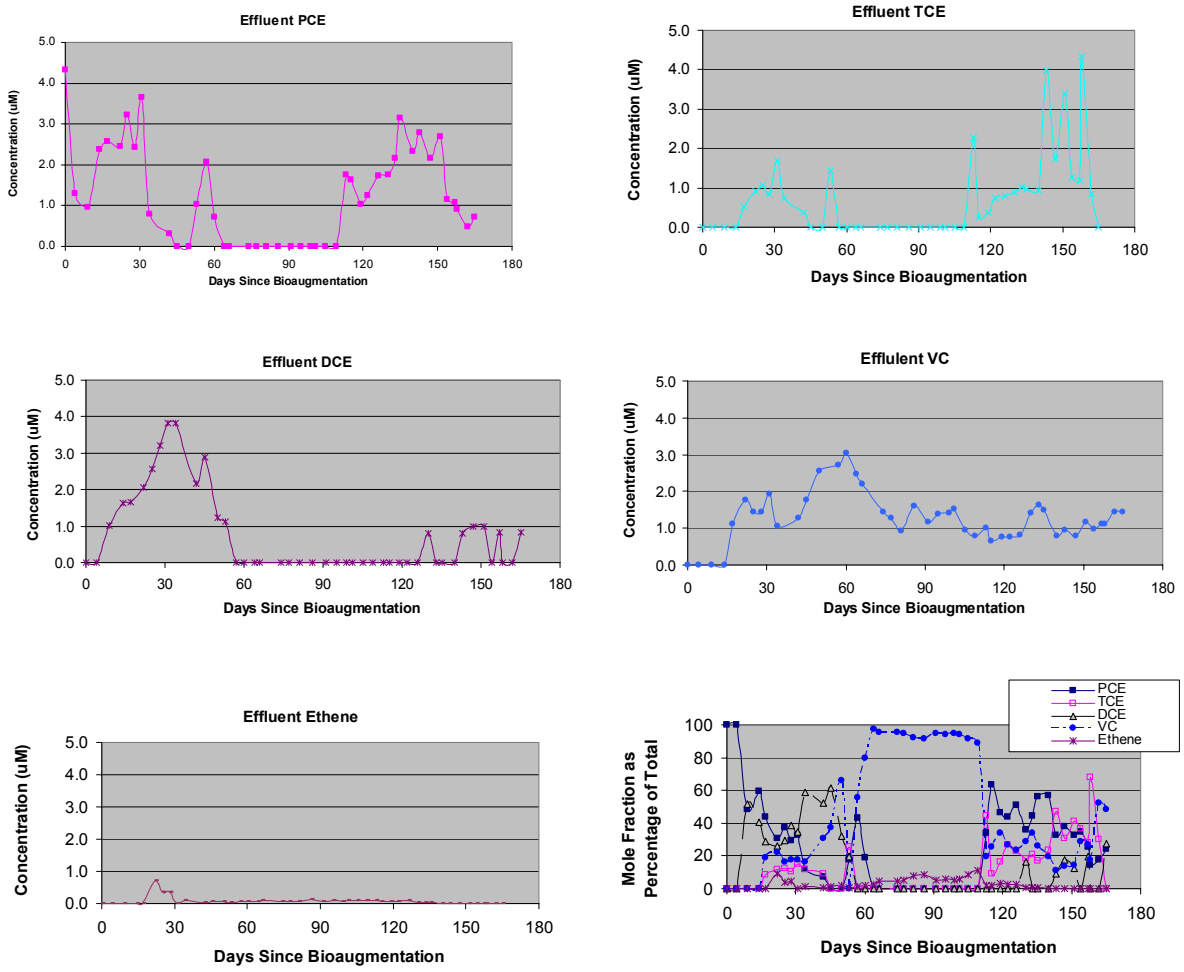


Figure 9. Chlorinated Constituents and Ethene in ECRS Tank Effluent

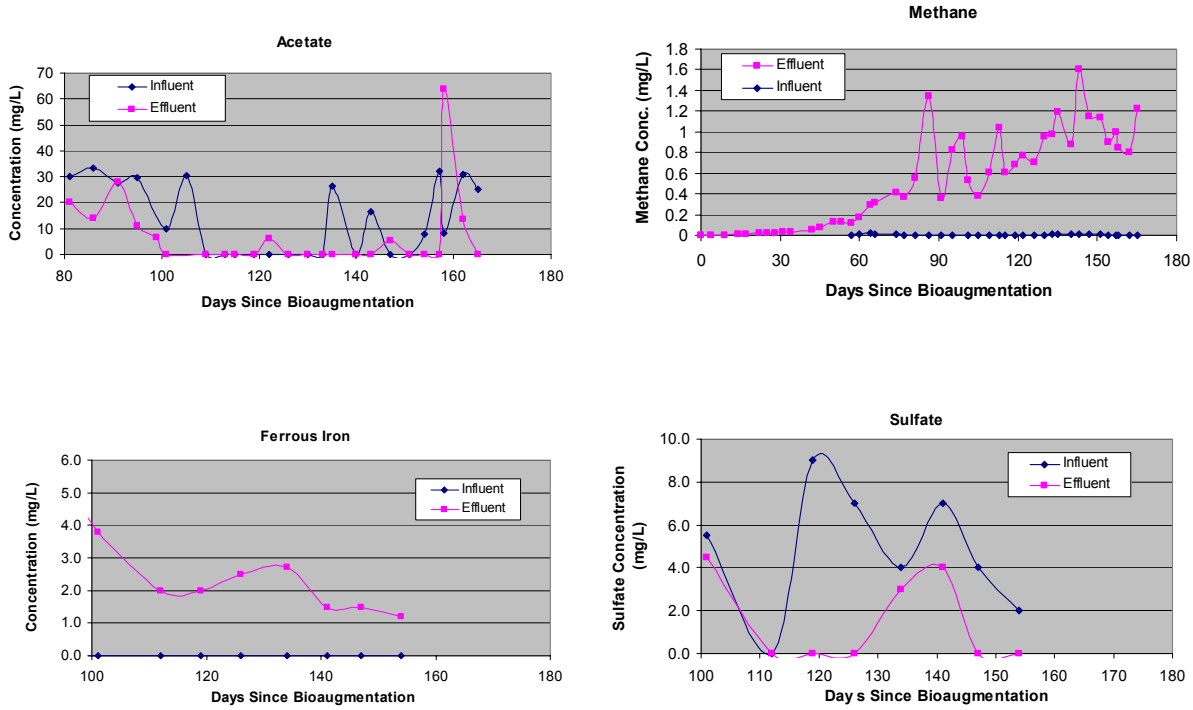


Figure 10. Geochemical Parameters and Acetate

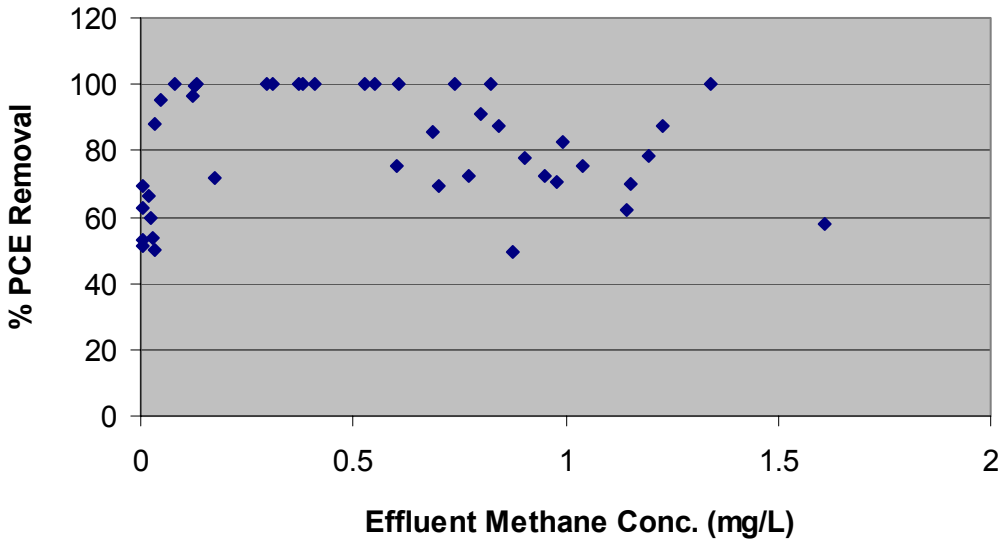


Figure 11. % PCE Removal vs. Effluent Methane Concentrations

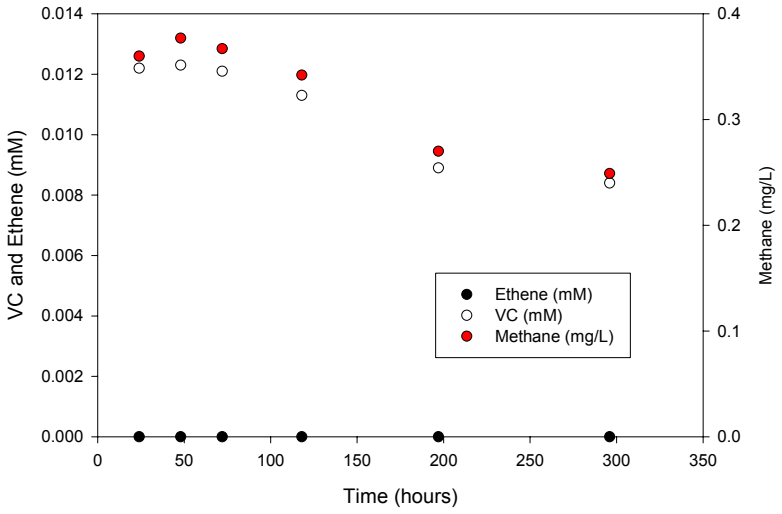


Figure 12. VC Oxidation Under Iron Reducing Conditions.

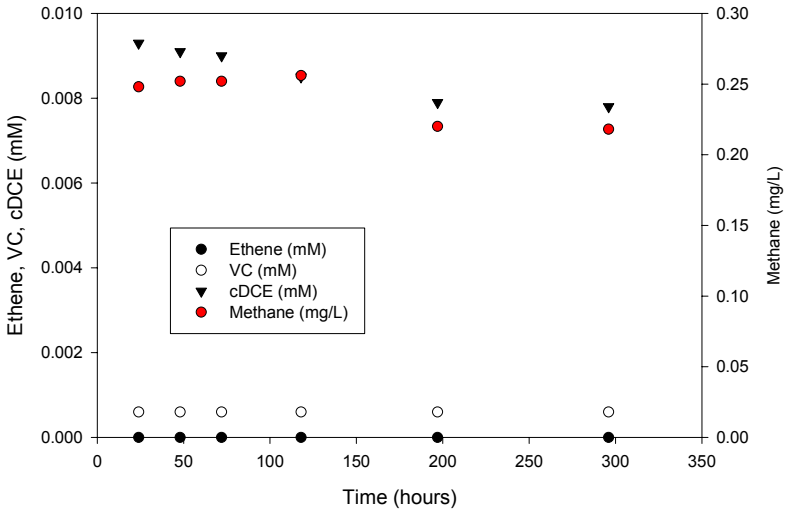


Figure 13. cDCE Oxidation Under Iron Reducing Conditions

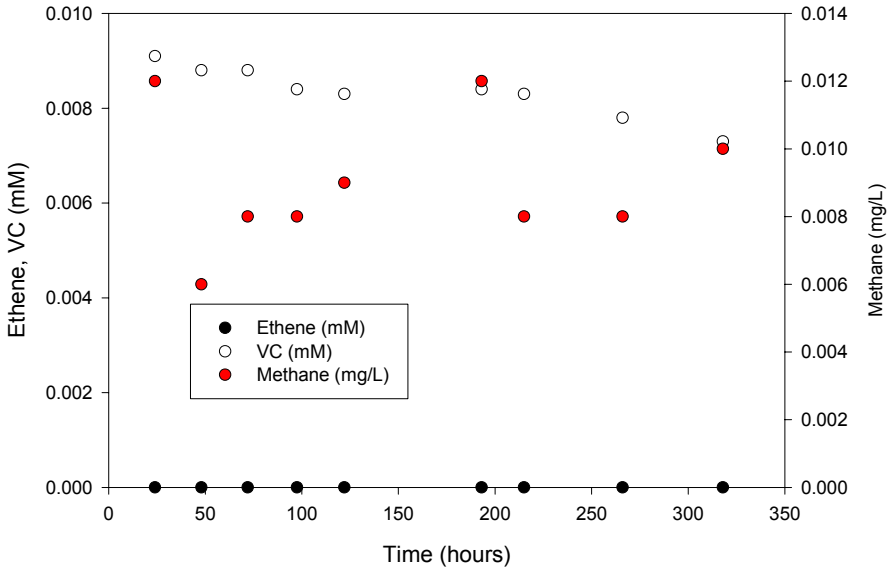


Figure 14. Deionized Water Control, 2mM Ferric Iron and 0.01 mM VC

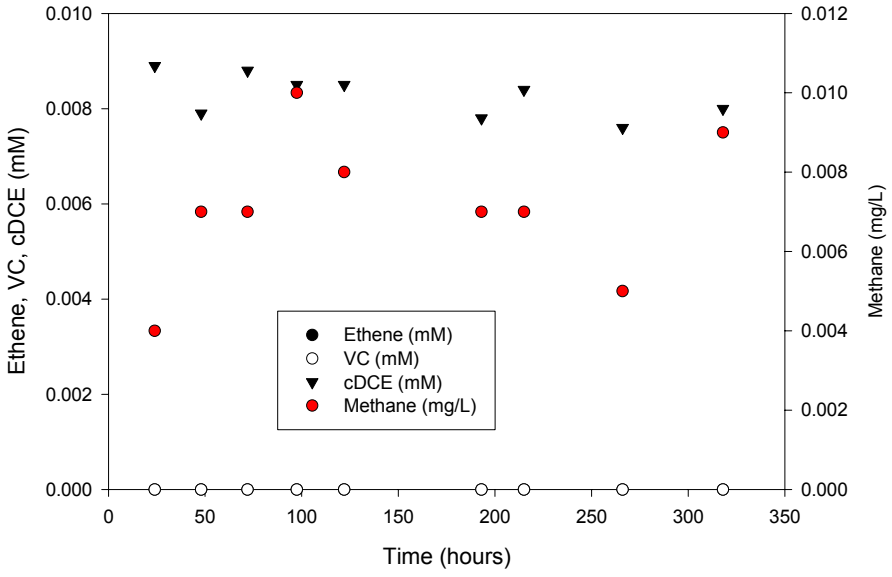
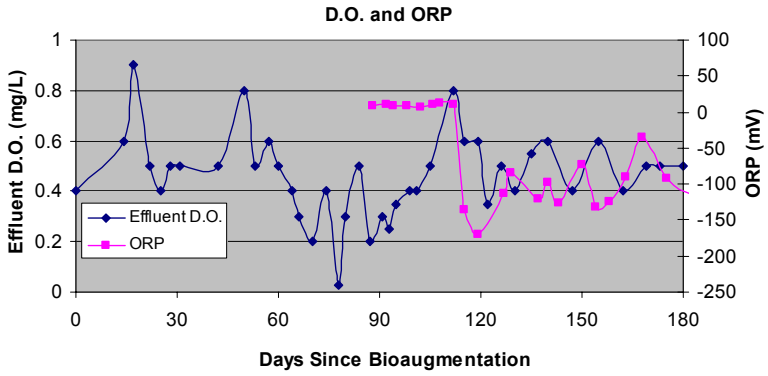
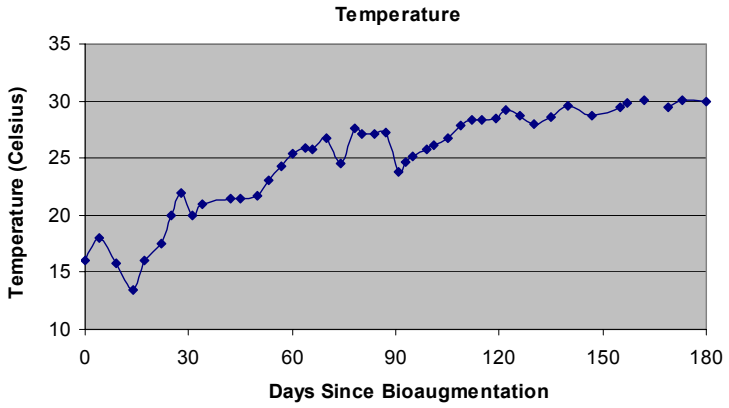


Figure 15. Deionized Water Control, 2mM Ferric Iron and 0.01 mM cDCE





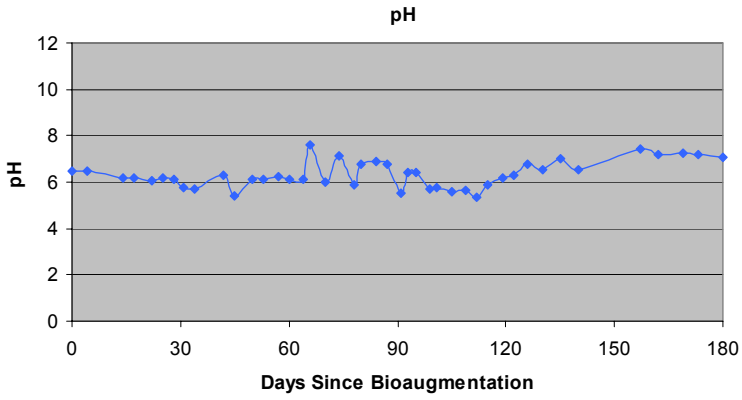
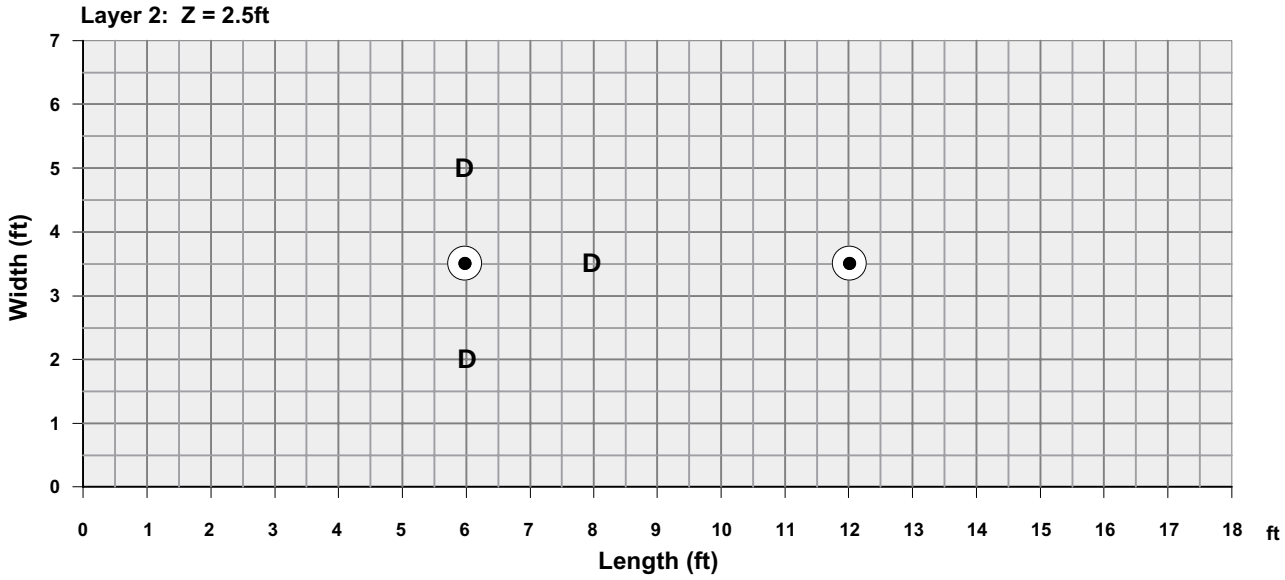


Figure 16. Monitoring Data for Dissolved Phase Experiment



LEGEND

⊙	Sparge well
D	DNAPL addition points

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Scale:	As Shown	**FIGURE 17**	

PCE DNAPL ADDITION LOCATIONS IN ECRS TANK

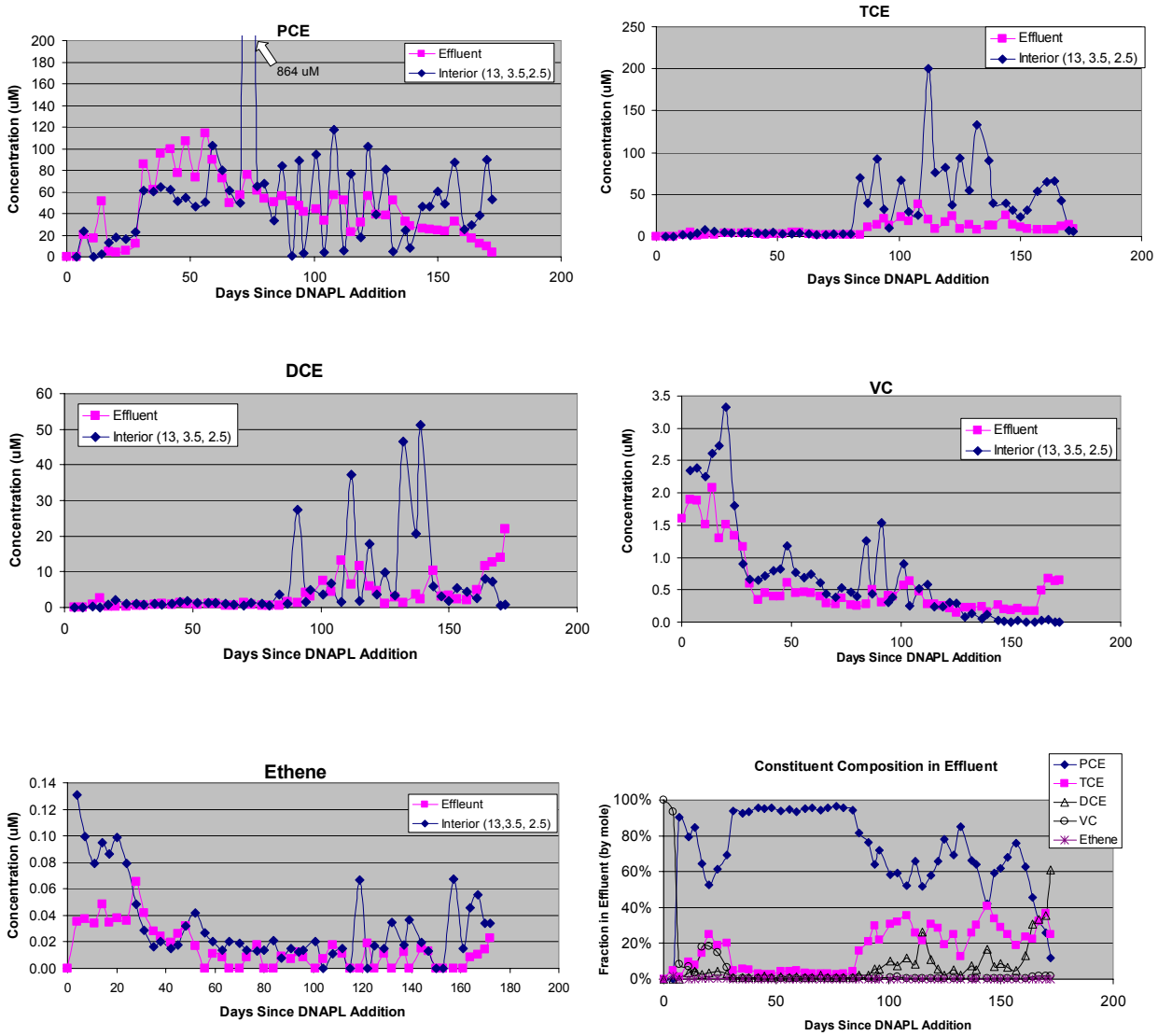


Figure 18. Volatile Organic Compound Data for DNAPL Experiment

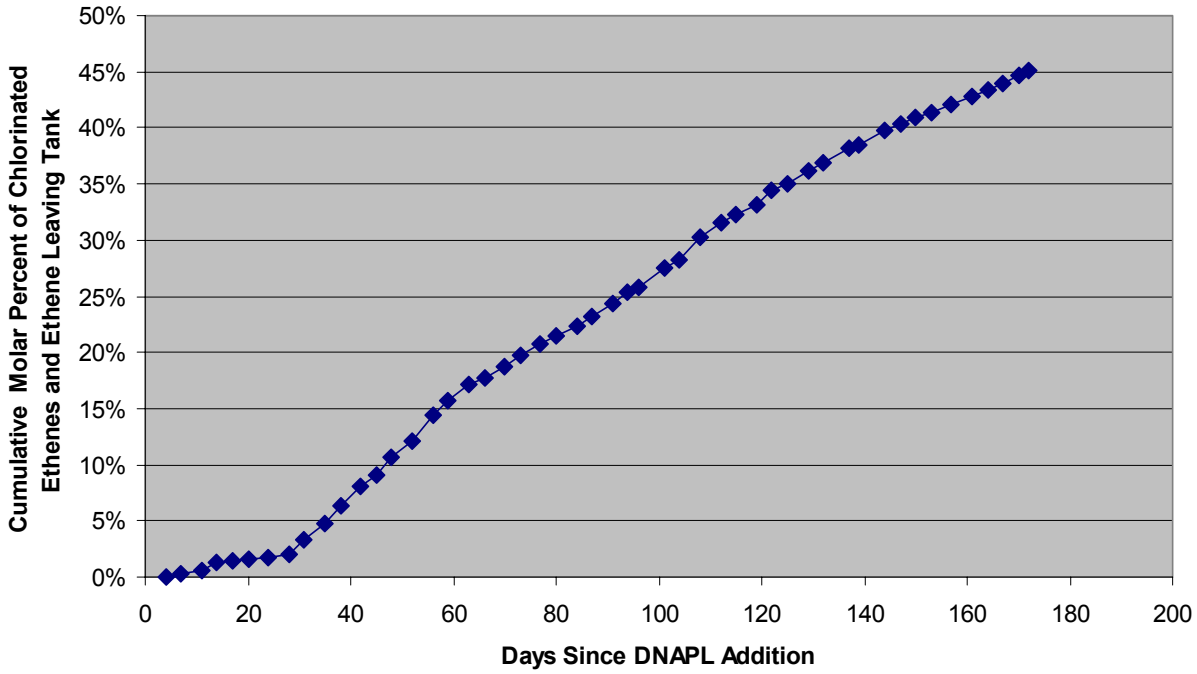
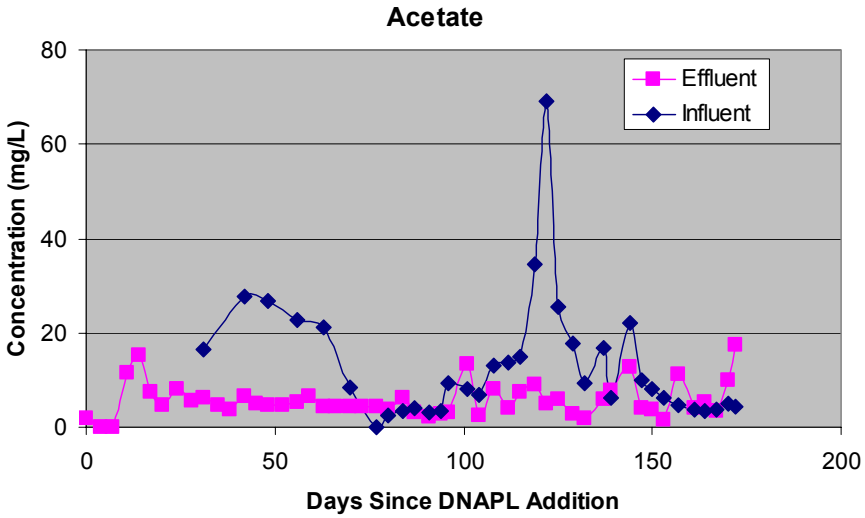


Figure 19. Cumulative Percent of Initial Moles Removed from Tank



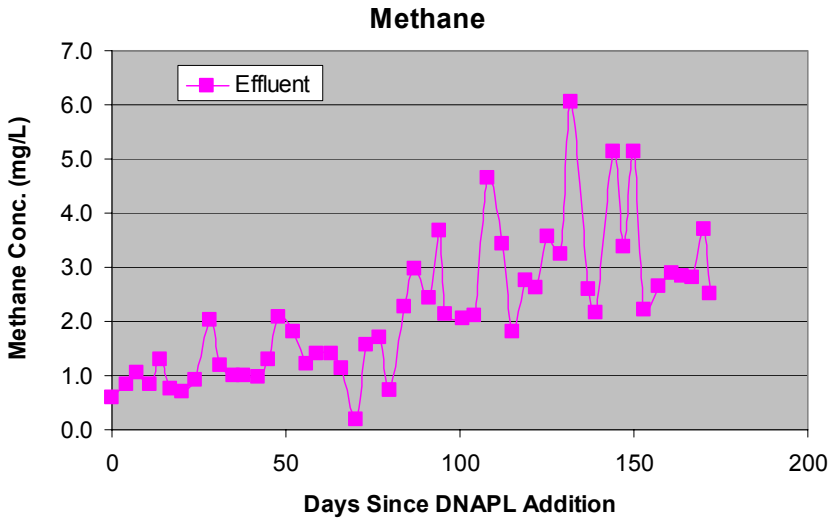


Figure 20. Acetate and Methane Concentrations in DNAPL Experiment

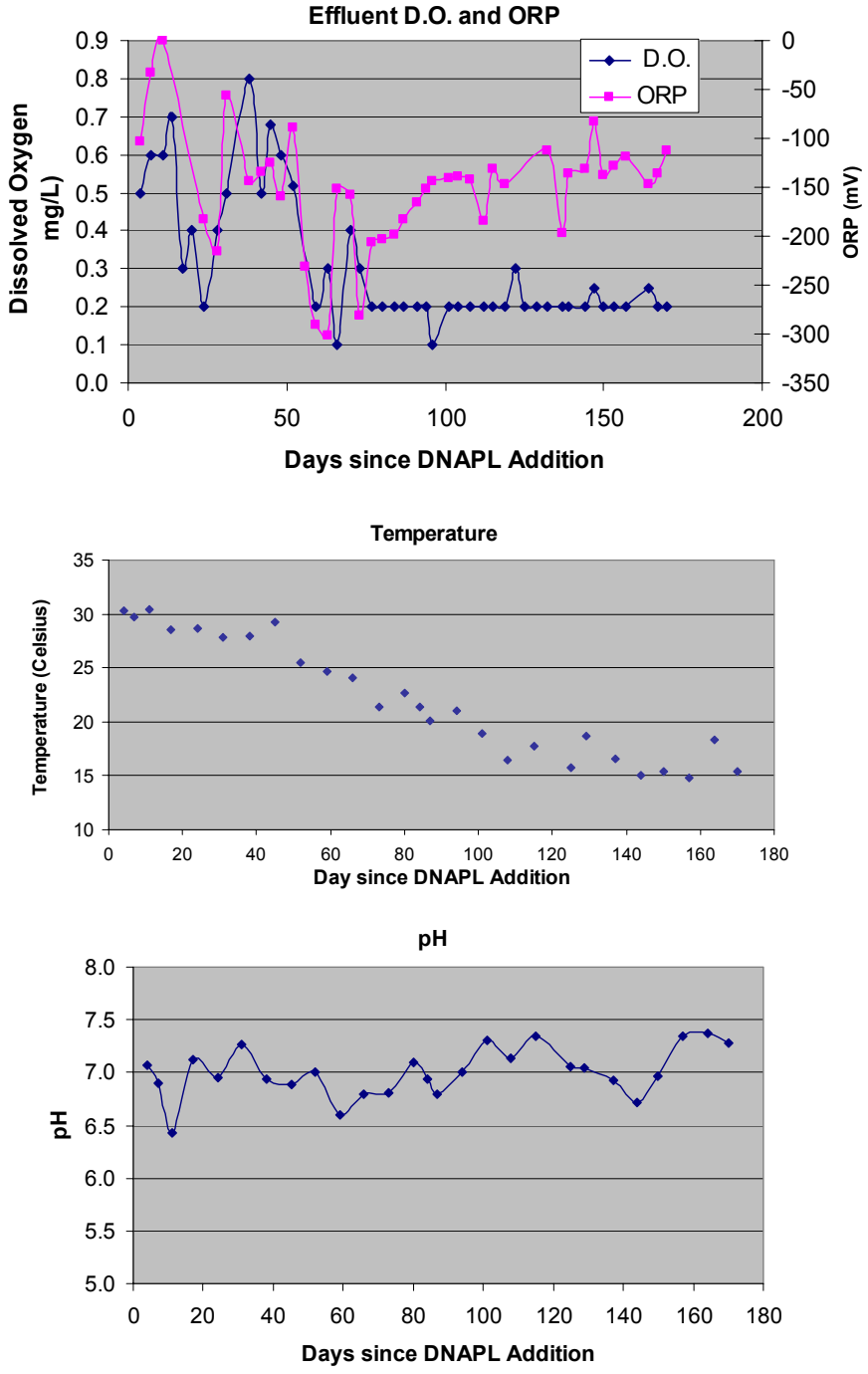


Figure 21. Effluent Monitoring Data for DNAPL Experiment

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GROUNDWATER
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FINAL REPORT FOR LOW-VOLUME PULSED BIOSPARGING OF HYDROGEN FOR BIOREMEDIATION OF CHLORINATED SOLVENT PLUMES

Groundwater Services, Inc., Houston, TX

APPENDICES

Appendix A: Distribution of Chlorinated Ethenes and Ethene within the ECRS Tank (Dissolved Phase Experiment)

Appendix B: Distribution of Methane and Acetate within the ECRS Tank (Dissolved Phase Experiment)

Appendix C: % Change in Gas Saturation Over Time in the ECRS Tank Using TDR

Appendix D: Data from Hydrogen Lifetime Experiments 1 and 2

Appendix E: Distribution of Chlorinated Ethenes and Ethene within the ECRS Tank (DNAPL Experiment)

Appendix F: Distribution of Methane and Acetate within the ECRS Tank (DNAPL Experiment)

GSI Job No. G-2535
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FINAL REPORT FOR LOW-VOLUME PULSED BIOSPARGING OF HYDROGEN FOR BIOREMEDIATION OF CHLORINATED SOLVENT PLUMES

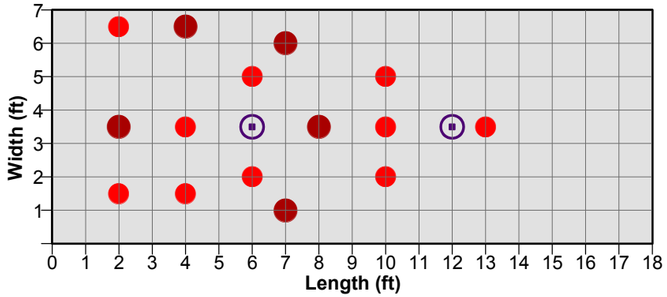
Groundwater Services, Inc., Houston, TX

APPENDIX A:

Distribution of Chlorinated Ethenes and Ethene within the ECRS Tank
(Dissolved Phase Experiment)

X-Y Plane (Z = 2.5 ft)

PCE



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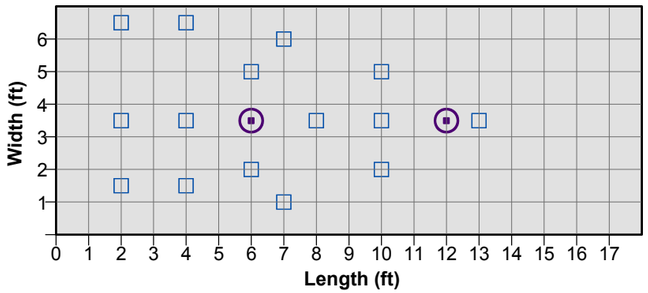
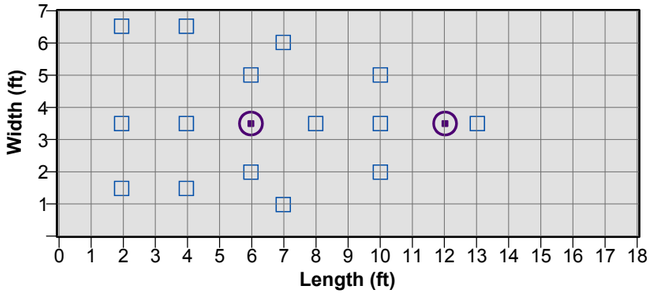


Water Flow

DCE



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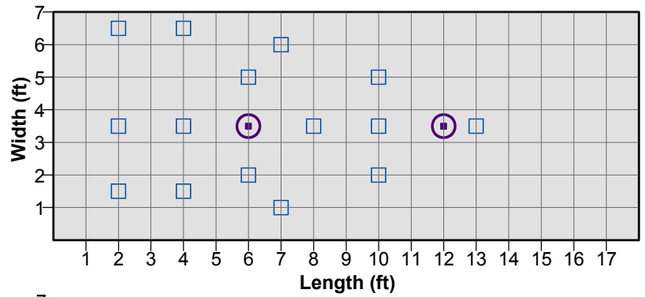
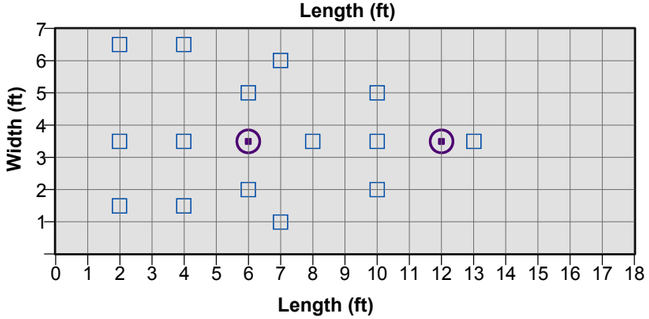
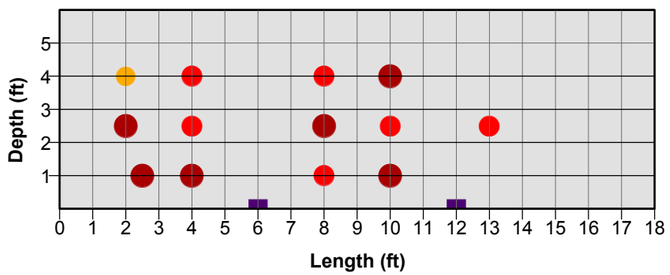


Ethene



X-Z Plane (Y = 3.5 ft)

PCE



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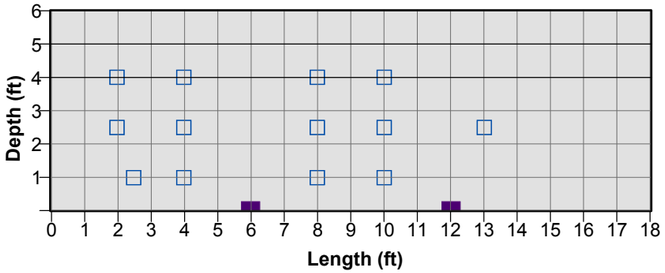

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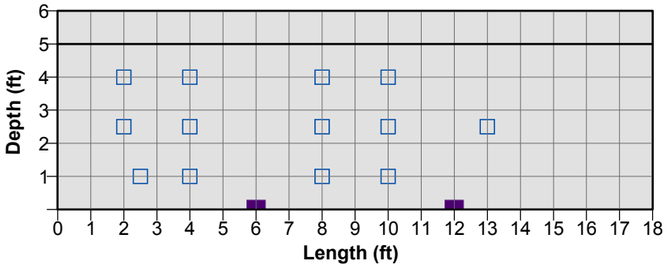

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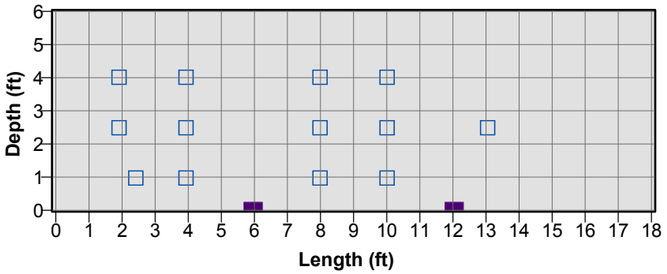
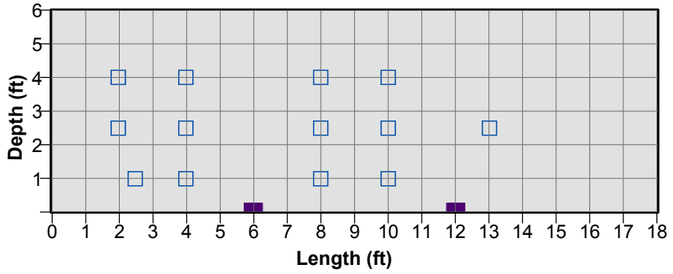


Ethene



Legend

Concentration (uM)

- ND
- > 0.001 - 0.1 uM
- > 0.1 - 0.5 uM
- > 0.5 - 1.0 uM
- > 1.0 - 2.0 uM
- > 2.0 - 4.0 uM
- > 4.0 - 6.0 uM
- > 6.0 uM
- Sparge Point X-Z Plane
- Sparge Point X-Y Plane

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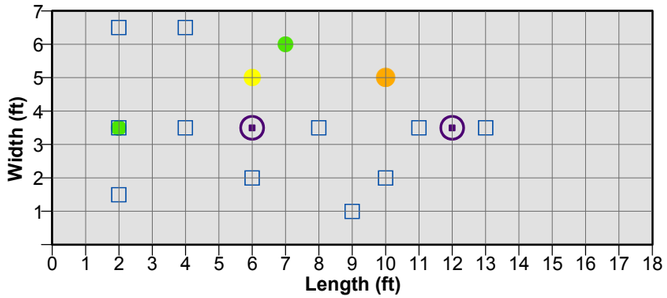
Aprv'd By:	CEA

FIGURE A.1

DISSOLVED PHASE EXPERIMENT
Chlorinated Ethenes + Ethene
February 18, 2002
(Before Bioaugmentation)
SERDP Hydrogen Biosparging Project

X-Y Plane (Z = 2.5 ft)

PCE



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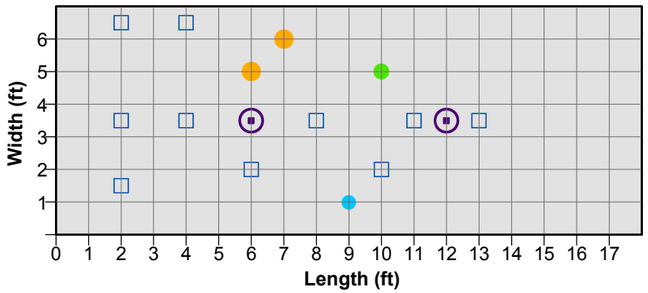

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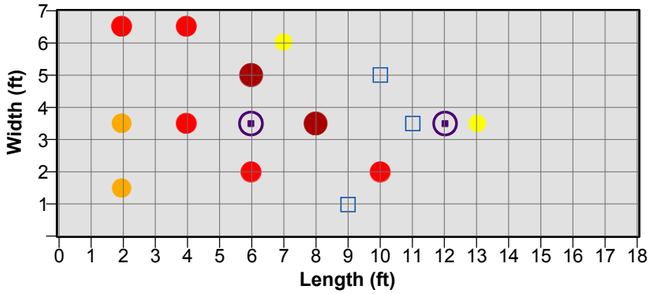

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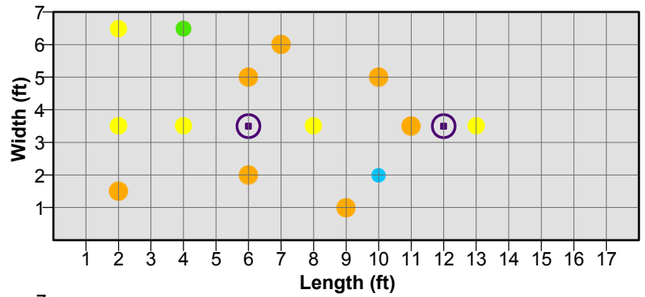
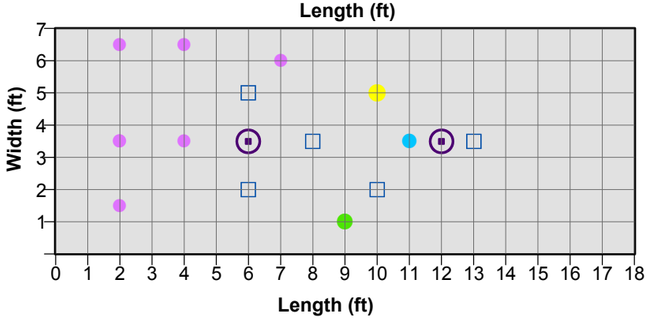


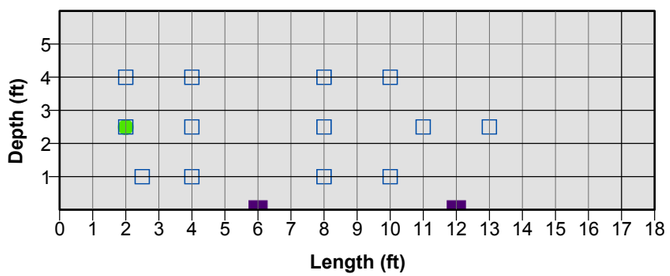
Ethene



Water Flow

X-Z Plane (Y = 3.5 ft)

PCE



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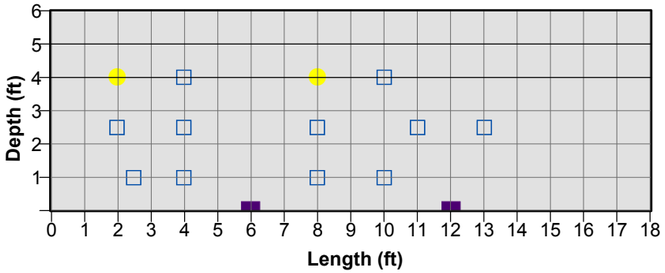

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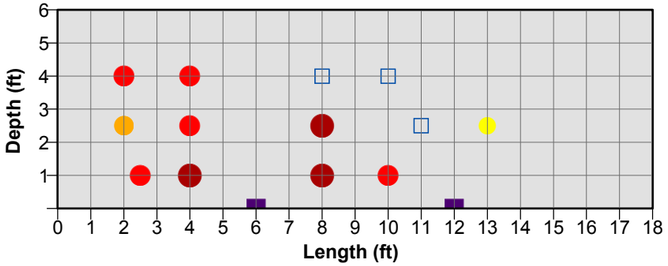

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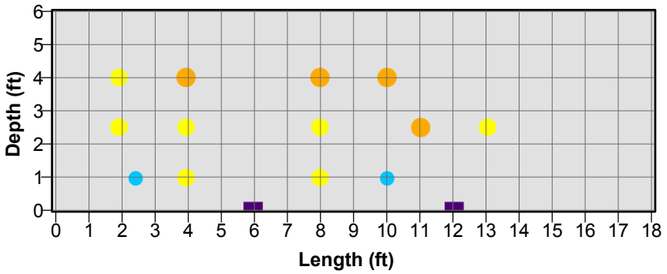

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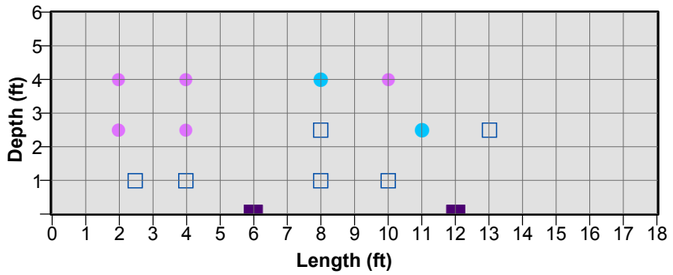

Legend

Concentration (uM)

- ND
- > 0.001 - 0.1 uM
- > 0.1 - 0.5 uM
- > 0.5 - 1.0 uM
- > 1.0 - 2.0 uM
- > 2.0 - 4.0 uM
- > 4.0 - 6.0 uM
- > 6.0 uM
- Sparge Point X-Z Plane
- Sparge Point X-Y Plane

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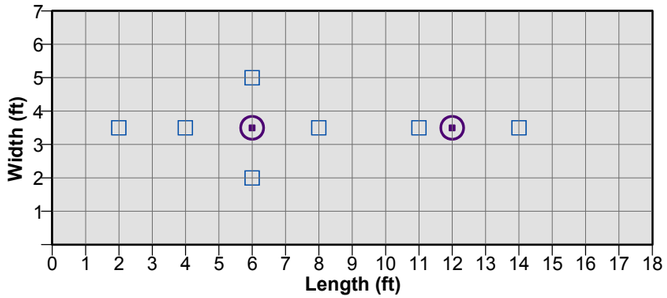
Aprv'd By:	CEA

FIGURE A.2

DISSOLVED PHASE EXPERIMENT
Chlorinated Ethenes + Ethene
March 24, 2002 (Day 62)
SERDP Hydrogen Biosparging Project

X-Y Plane (Z = 2.5 ft)

PCE



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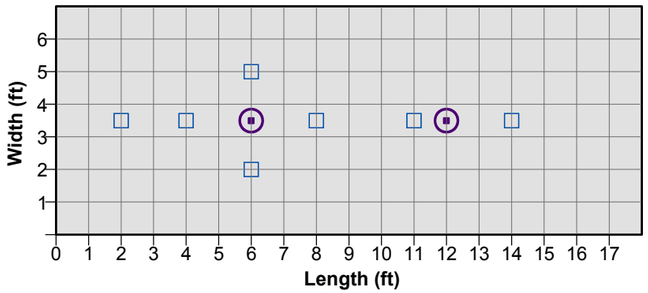

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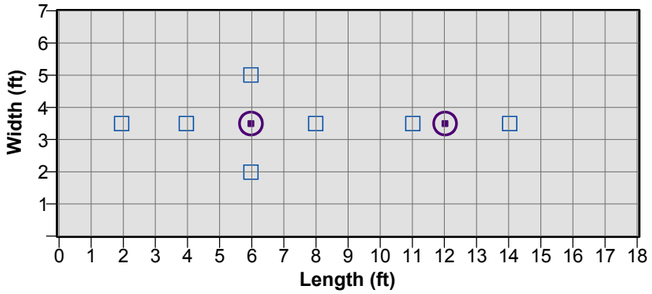
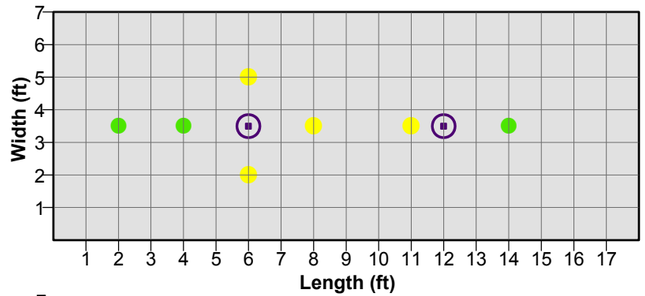
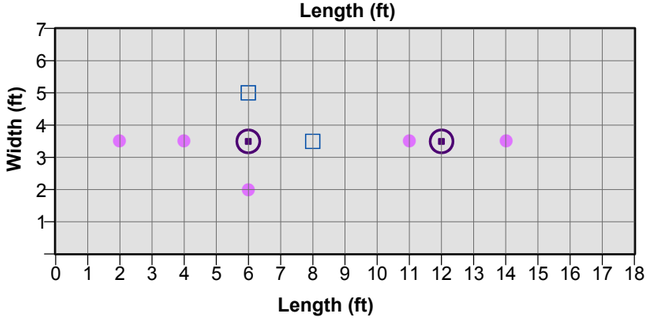


Water Flow

VC

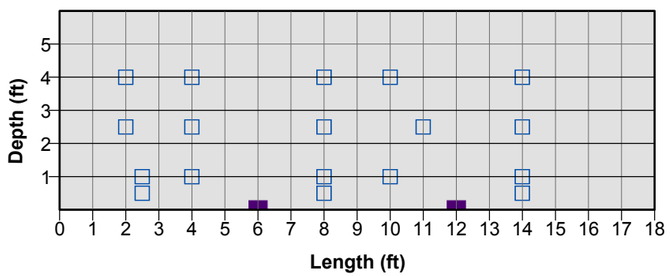


Ethene



X-Z Plane (Y = 3.5 ft)

PCE



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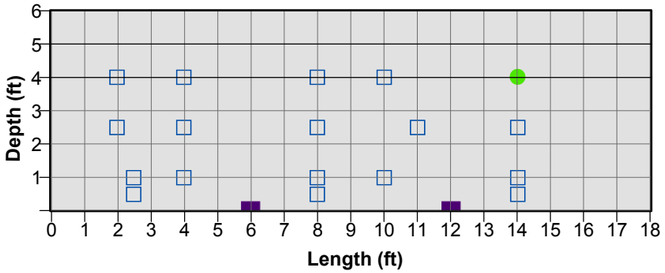

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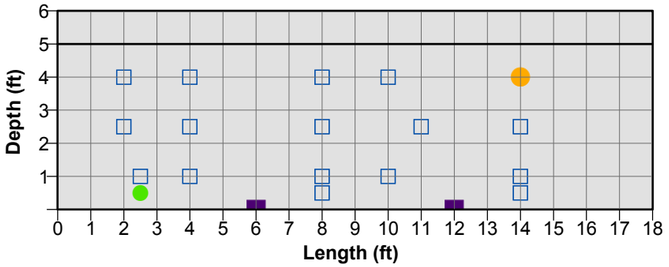

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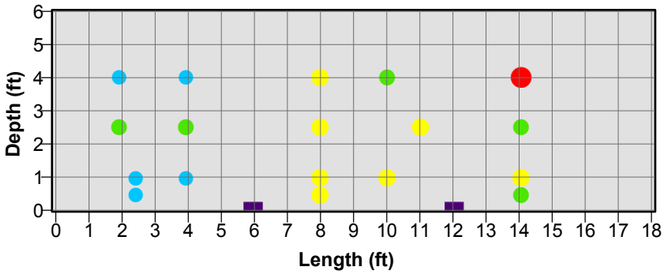
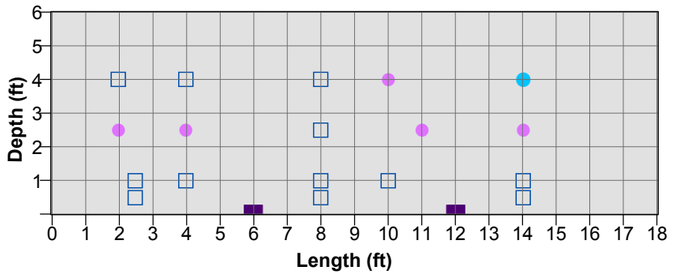


Ethene



Legend

Concentration (uM)

- ND
- > 0.001 - 0.1 uM
- > 0.1 - 0.5 uM
- > 0.5 - 1.0 uM
- > 1.0 - 2.0 uM
- > 2.0 - 4.0 uM
- > 4.0 - 6.0 uM
- > 6.0 uM
- Sparge Point X-Z Plane
- Sparge Point X-Y Plane

GROUNDWATER SERVICES, INC.

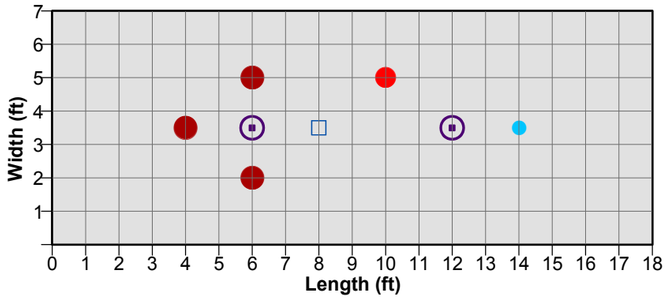
GSI Job No.	G-2535-107
Issued:	7/16/03
Revised:	---------
Scale:	As Shown
Drawn By:	JJA
Chk'd By:	CEA
Aprv'd By:	CEA

FIGURE A.3

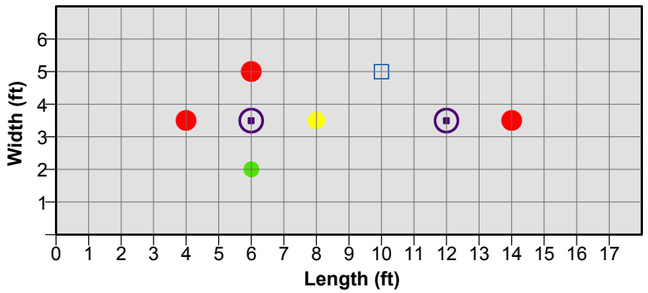
DISSOLVED PHASE EXPERIMENT
Chlorinated Ethenes + Ethene
May 6, 2002 (Day 105)
SERDP Hydrogen Biosparging Project

X-Y Plane (Z = 2.5 ft)

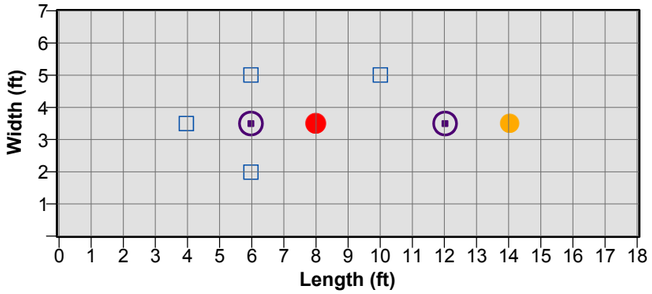
PCE



TCE

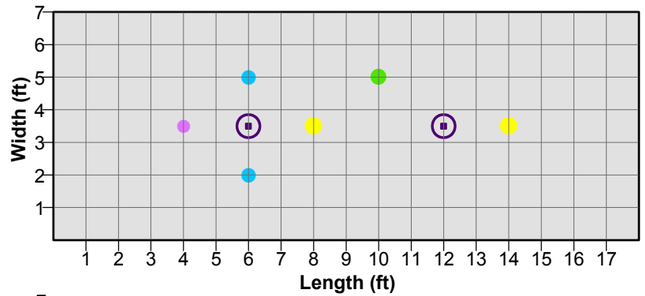


DCE

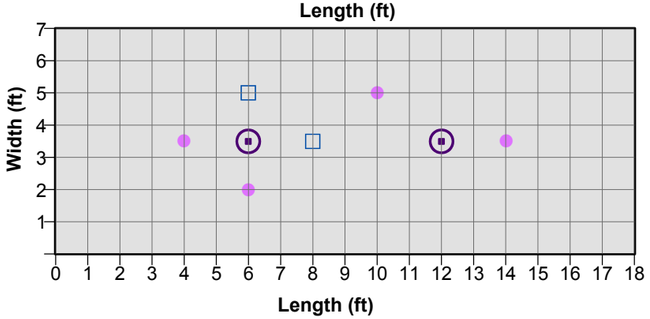


Water Flow

VC

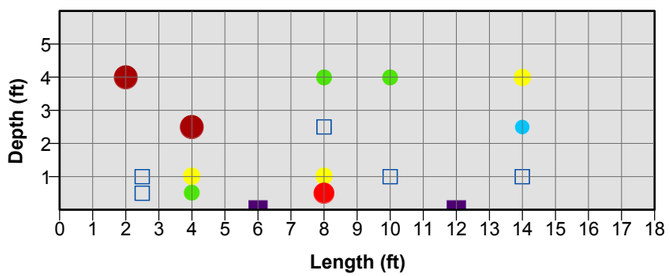


Ethene



X-Z Plane (Y = 3.5 ft)

PCE



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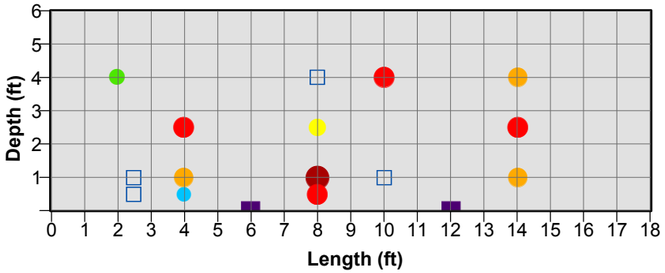
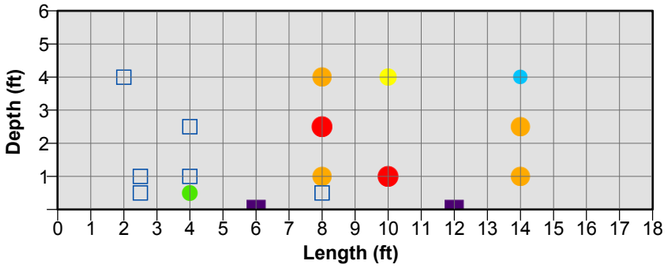
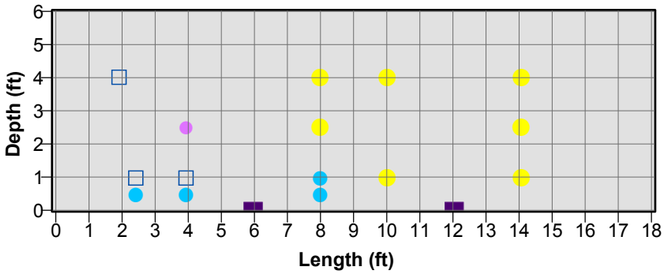


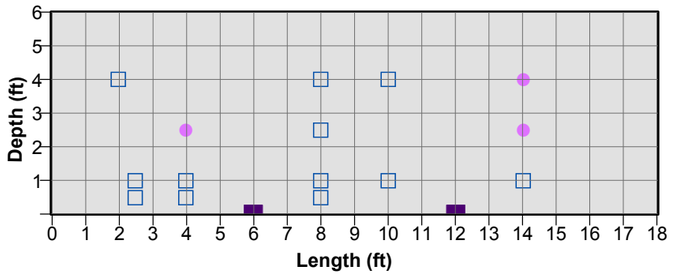
DCE



VC



Ethene



Legend

Concentration (uM)

- ND
- > 0.001 - 0.1 uM
- > 0.1 - 0.5 uM
- > 0.5 - 1.0 uM
- > 1.0 - 2.0 uM
- > 2.0 - 4.0 uM
- > 4.0 - 6.0 uM
- > 6.0 uM
- Sparge Point X-Z Plane
- Sparge Point X-Y Plane

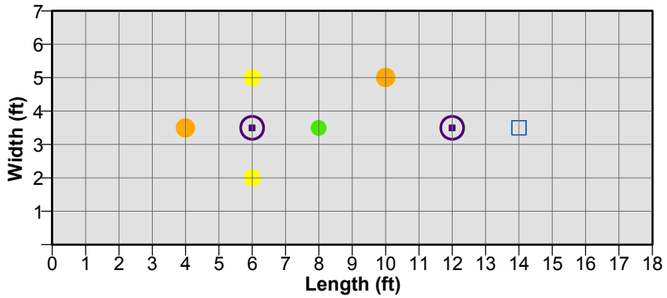
GROUNDWATER SERVICES, INC.

GSI Job No.	G-2535-107	Drawn By:	JJA
Issued:	7/16/03	Chk'd By:	CEA
Revised:	---------	Aprv'd By:	CEA
Scale:	As Shown	FIGURE A.4	

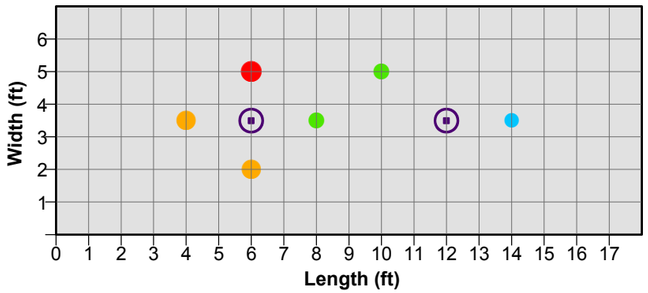
DISSOLVED PHASE EXPERIMENT
Chlorinated Ethenes + Ethene
July 11, 2002 (Day 171)
SERDP Hydrogen Biosparging Project

X-Y Plane (Z = 2.5 ft)

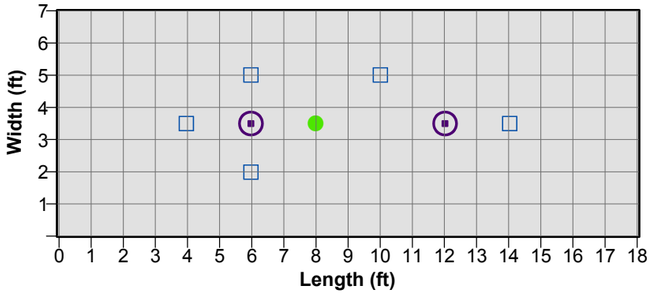
PCE



TCE

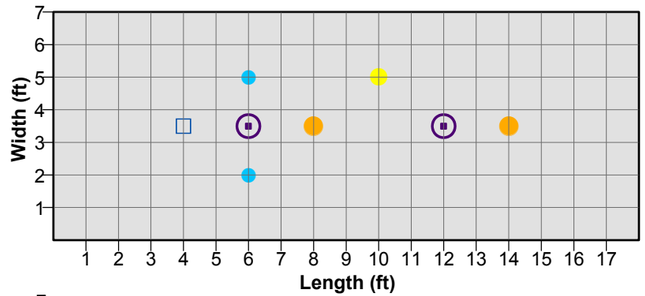


DCE

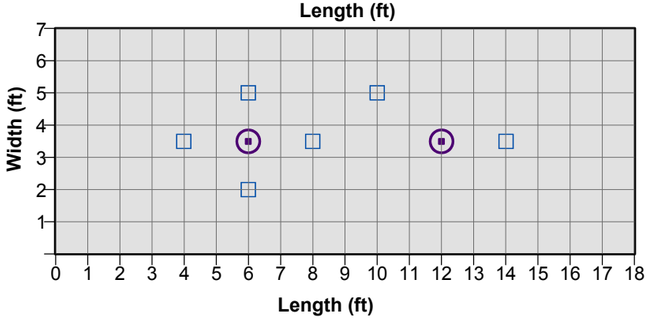


Water Flow

VC

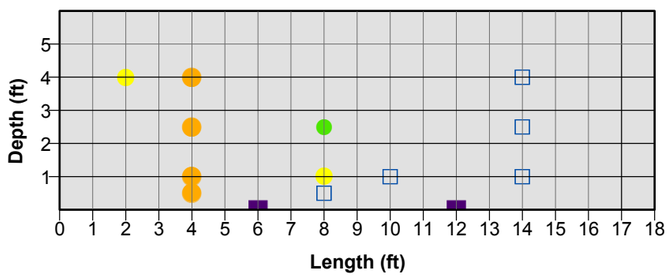


Ethene



X-Z Plane (Y = 3.5 ft)

PCE



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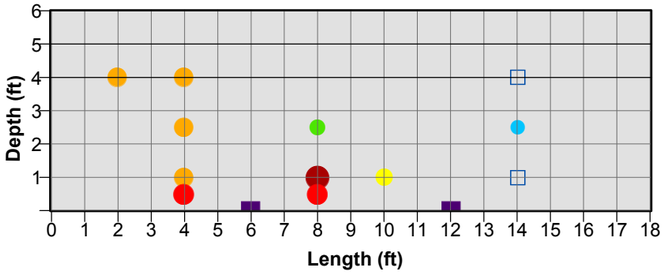
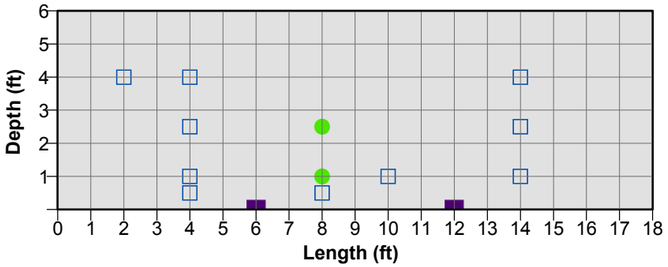
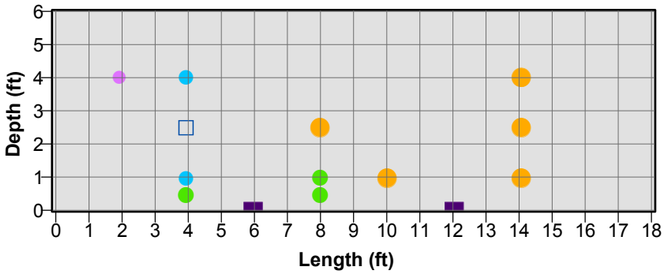


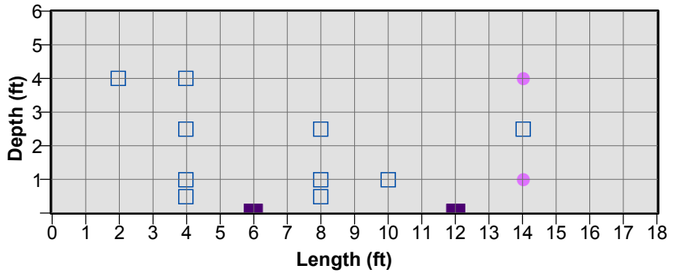
DCE



VC



Ethene



Legend

Concentration (uM)

- ND
- > 0.001 - 0.1 uM
- > 0.1 - 0.5 uM
- > 0.5 - 1.0 uM
- > 1.0 - 2.0 uM
- > 2.0 - 4.0 uM
- > 4.0 - 6.0 uM
- > 6.0 uM
- Sparge Point X-Z Plane
- Sparge Point X-Y Plane

GROUNDWATER SERVICES, INC.

GSI Job No.	G-2535-107	Drawn By:	JJA
Issued:	7/16/03	Chk'd By:	CEA
Revised:	---------	Aprv'd By:	CEA
Scale:	As Shown	FIGURE A.5	

DISSOLVED PHASE EXPERIMENT
Chlorinated Ethenes + Ethene
August 5, 2002 (Day 193)
SERDP Hydrogen Biosparging Project

GSI Job No. G-2535
Issued: October 7, 2003

GROUNDWATER
SERVICES, INC.

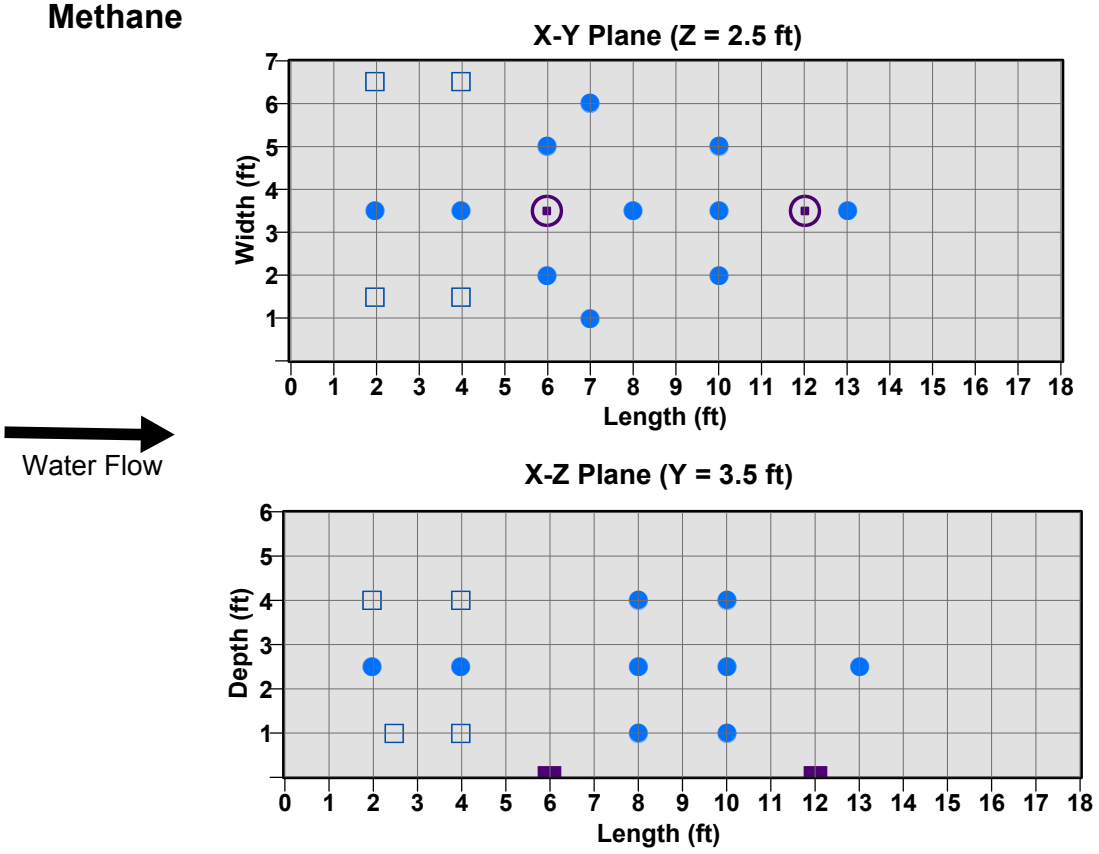
FINAL REPORT FOR LOW-VOLUME PULSED BIOSPARGING OF HYDROGEN FOR BIOREMEDIATION OF CHLORINATED SOLVENT PLUMES

Groundwater Services, Inc., Houston, TX

APPENDIX B:

Distribution of Methane and Acetate within the ECRS Tank
(Dissolved Phase Experiment)

Methane



Legend

Methane Concentration

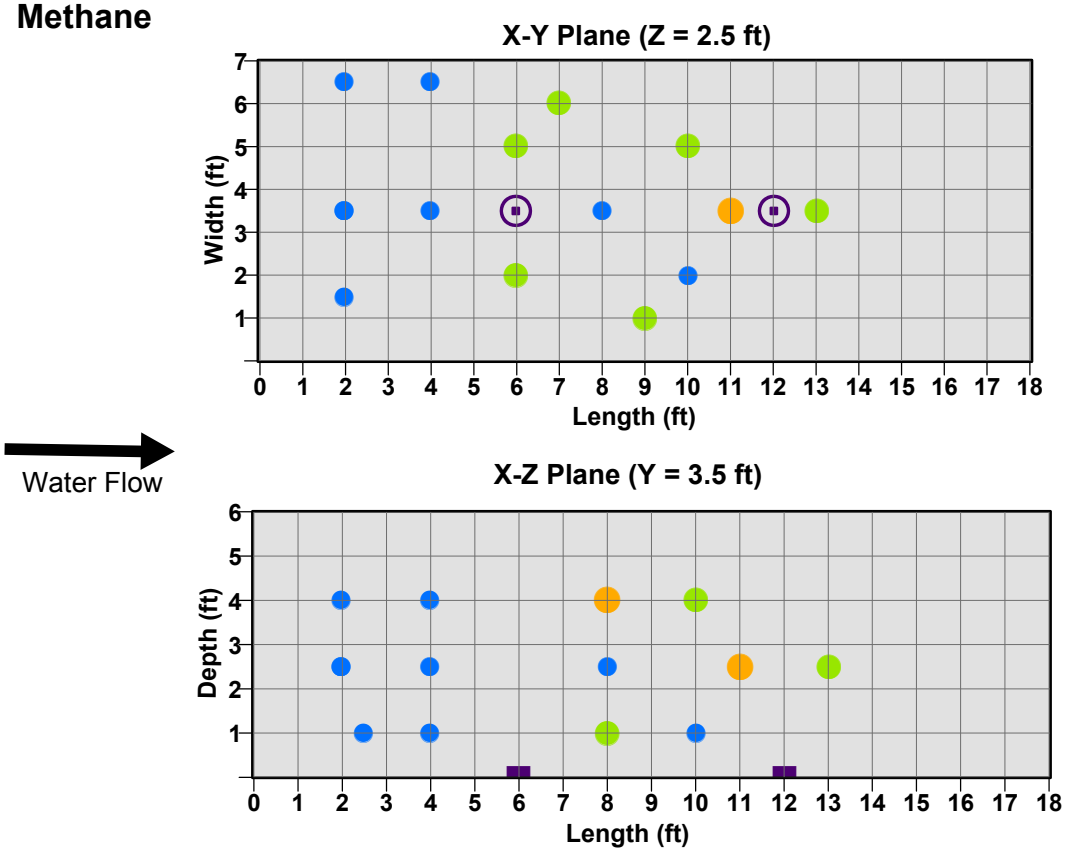
- ND
- <= 0.1 mg/L
- > 0.1 - 5.0 mg/L
- > 5.0 - 10.0 mg/L
- > 10.0 mg/L
- Sparge Point X-Y Plane
- Sparge Point X-Z Plane

GROUNDWATER SERVICES, INC.

GSI Job No.	G-2535-107	Drawn By:	JJA
Issued:	7/16/03	Chk'd By:	CEA
Revised:	---------	Aprv'd By:	CEA
Scale:	As Shown	**FIGURE B.1**	

Dissolved Phase Experiment
Methane and Acetate
February 18, 2002
(Before Bioaugmentation)
SERDP Hydrogen Biosparging Project

Methane



Legend

Methane Concentration

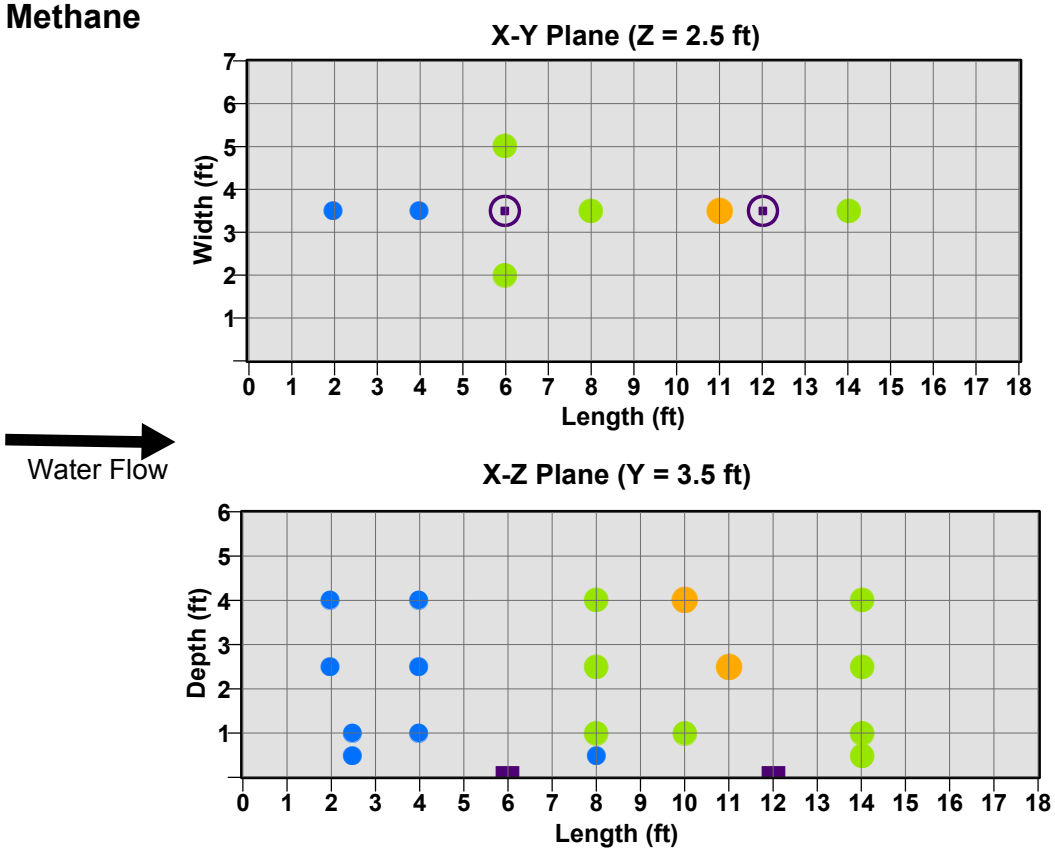
- ND
- <= 0.1 mg/L
- > 0.1 - 5.0 mg/L
- > 5.0 - 10.0 mg/L
- > 10.0 mg/L
- Sparge Point X-Y Plane
- Sparge Point X-Z Plane

GROUNDWATER SERVICES, INC.

GSI Job No.	G-2535-107	Drawn By:	JJA
Issued:	7/16/03	Chk'd By:	CEA
Revised:	---------	Aprv'd By:	CEA
Scale:	As Shown	**FIGURE B.2**	

Dissolved Phase Experiment
Methane and Acetate
March 24, 2002 (Day 62)
SERDP Hydrogen Biosparging Project

Methane



Legend

Methane Concentration

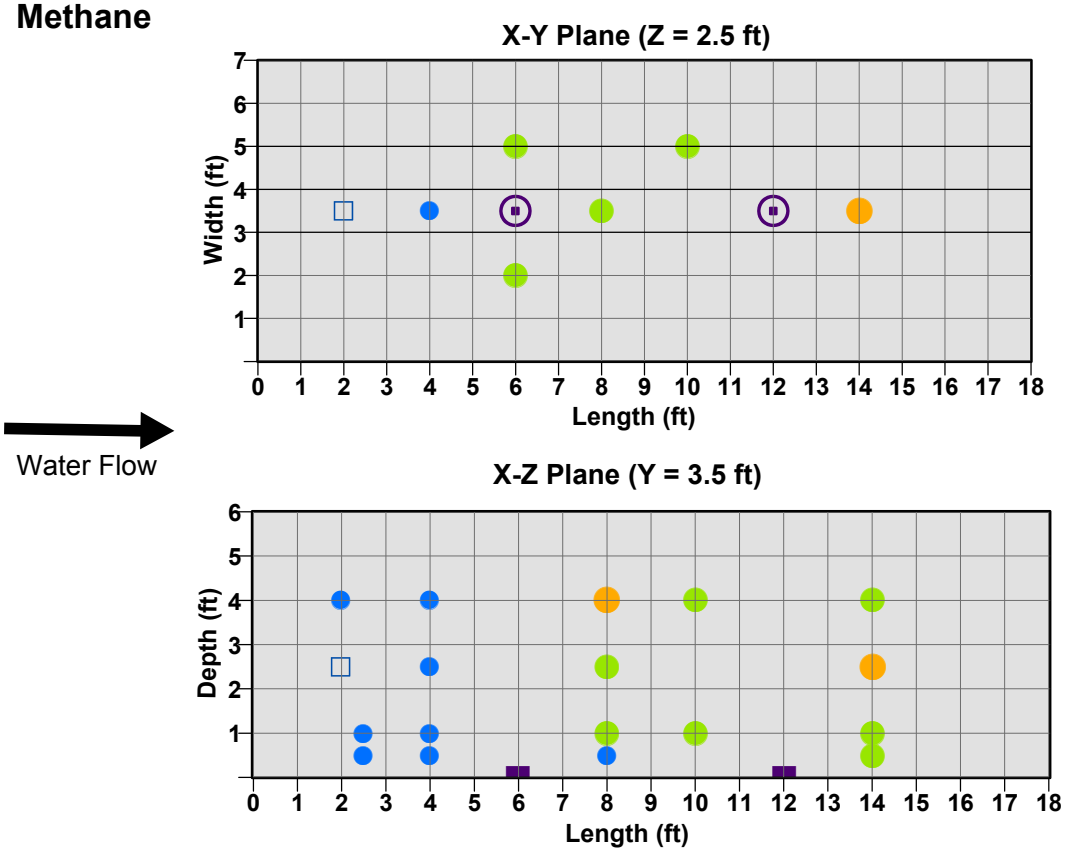
- ND
- <= 0.1 mg/L
- > 0.1 - 5.0 mg/L
- > 5.0 - 10.0 mg/L
- > 10.0 mg/L
- Sparge Point X-Y Plane
- Sparge Point X-Z Plane

GROUNDWATER SERVICES, INC.

GSI Job No.	G-2535-107	Drawn By:	JJA
Issued:	7/16/03	Chk'd By:	CEA
Revised:	---------	Aprv'd By:	CEA
Scale:	As Shown	**FIGURE B.3**	

Dissolved Phase Experiment
Methane and Acetate
May 6, 2002 (Day 105)
SERDP Hydrogen Biosparging Project

Methane

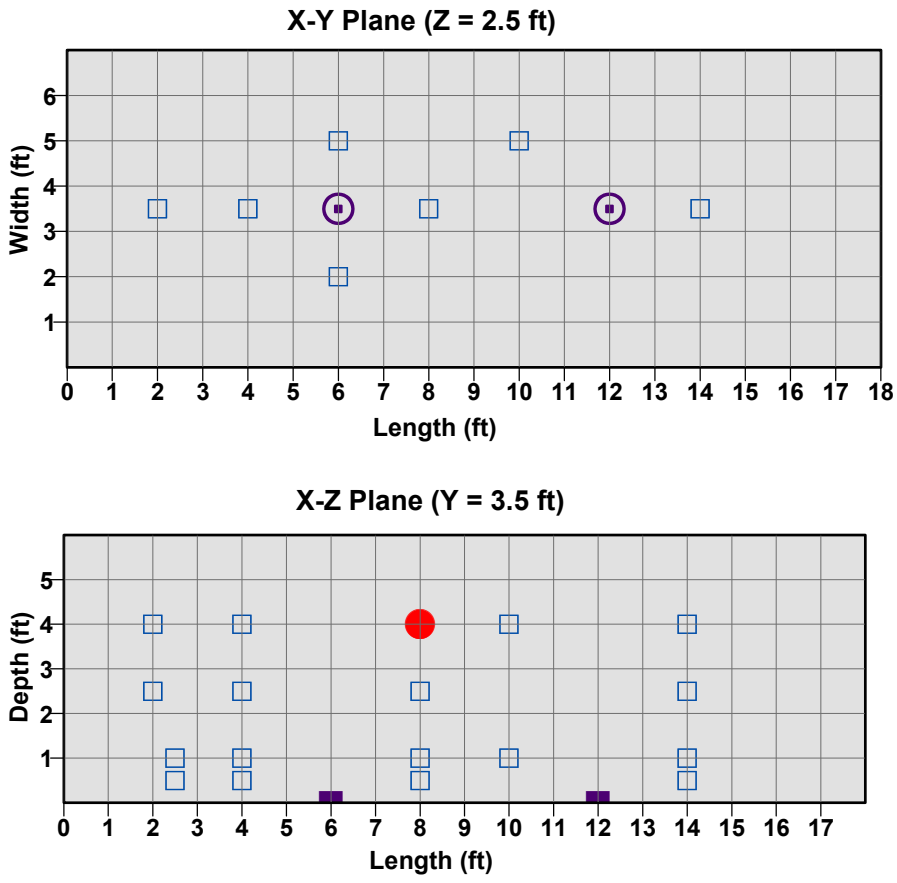


Legend

Methane Concentration

- ND
- <= 0.1 mg/L
- > 0.1 - 5.0 mg/L
- > 5.0 - 10.0 mg/L
- > 10.0 mg/L
- Sparge Point X-Y Plane
- Sparge Point X-Z Plane

Acetate



Legend

Acetate Concentration

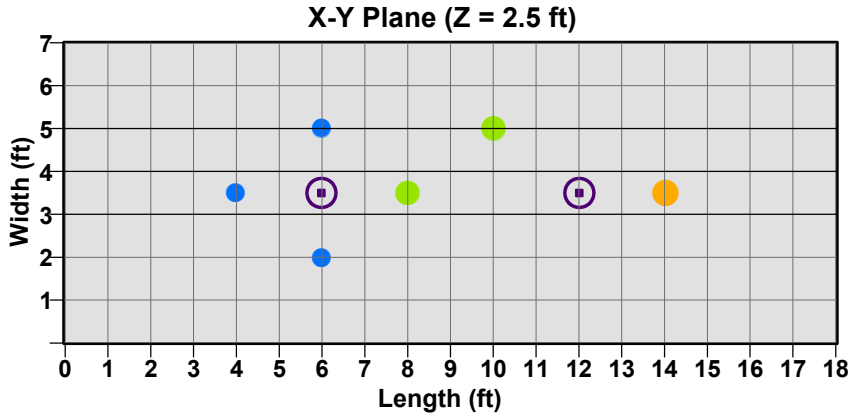
- ND
- <= 0.1 mg/L
- > 0.1 - 10.0 mg/L
- > 10.0 - 50.0 mg/L
- > 50.0 mg/L
- Sparge Point X-Y Plane
- Sparge Point X-Z Plane

GROUNDWATER SERVICES, INC.

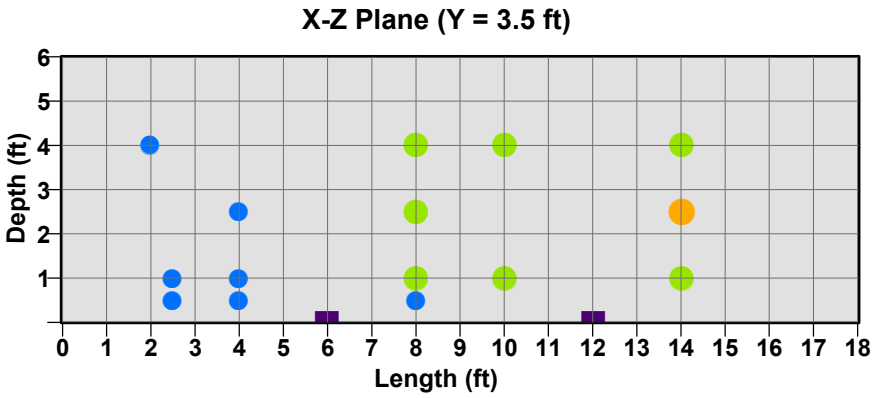
GSI Job No.	G-2535-107	Drawn By:	JJA
Issued:	7/16/03	Chk'd By:	CEA
Revised:	---------	Aprv'd By:	CEA
Scale:	As Shown	FIGURE B.4	

Dissolved Phase Experiment
Methane and Acetate
June 11, 2002 (Day 141)
SERDP Hydrogen Biosparging Project

Methane



Water Flow

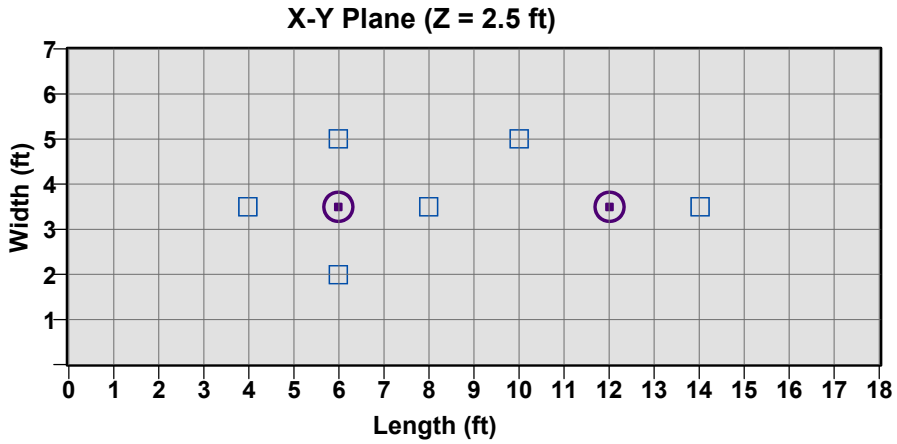


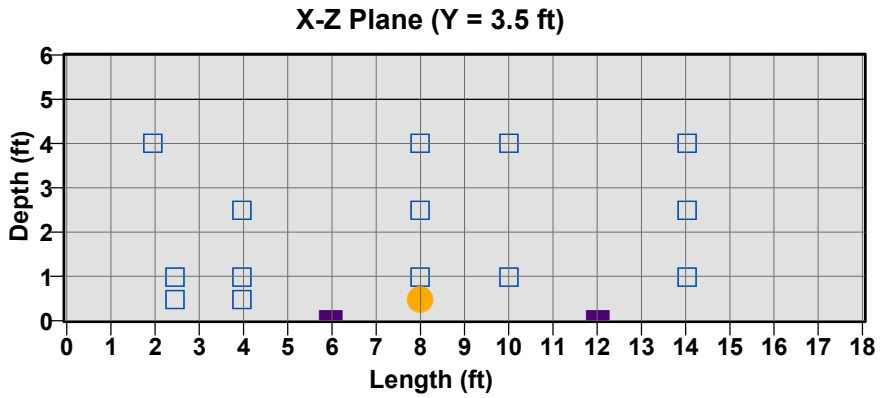
Legend

Methane Concentration

- ND
- <= 0.1 mg/L
- > 0.1 - 5.0 mg/L
- > 5.0 - 10.0 mg/L
- > 10.0 mg/L
- Sparge Point X-Y Plane
- Sparge Point X-Z Plane

Acetate





Legend

Acetate Concentration

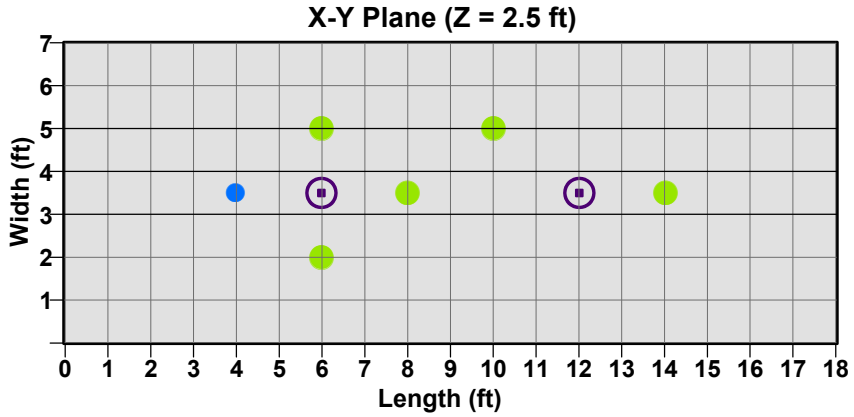
- ND
- <= 0.1 mg/L
- > 0.1 - 10.0 mg/L
- > 10.0 - 50.0 mg/L
- > 50.0 mg/L
- Sparge Point X-Y Plane
- Sparge Point X-Z Plane

GROUNDWATER SERVICES, INC.

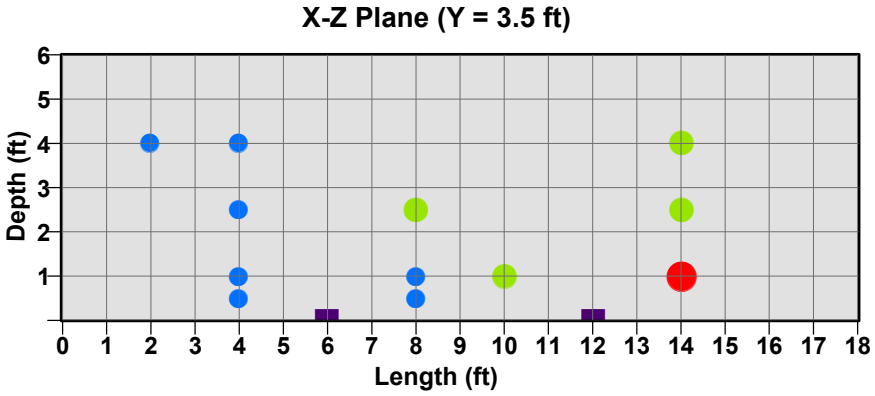
GSI Job No.	G-2535-107	Drawn By:	JJA
Issued:	7/16/03	Chk'd By:	CEA
Revised:	---------	Aprv'd By:	CEA
Scale:	As Shown	FIGURE B.5	

Dissolved Phase Experiment
Methane and Acetate
July 11, 2002 (Day 171)
SERDP Hydrogen Biosparging Project

Methane



Water Flow

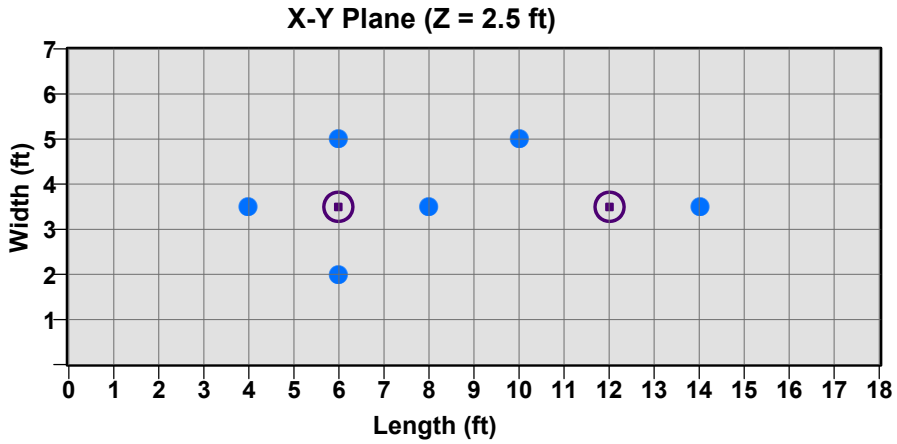


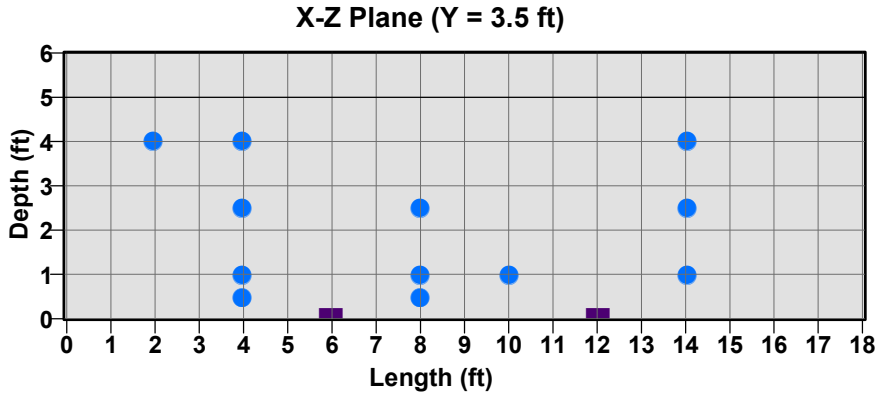
Legend

Methane Concentration

- ND
- <= 0.1 mg/L
- > 0.1 - 5.0 mg/L
- > 5.0 - 10.0 mg/L
- > 10.0 mg/L
- Sparge Point X-Y Plane
- Sparge Point X-Z Plane

Acetate





Legend

Acetate Concentration

- ND
- <= 0.1 mg/L
- > 0.1 - 10.0 mg/L
- > 10.0 - 50.0 mg/L
- > 50.0 mg/L
- Sparge Point X-Y Plane
- Sparge Point X-Z Plane

GROUNDWATER SERVICES, INC.

GSI Job No.	G-2535-107	Drawn By:	JJA
Issued:	7/16/03	Chk'd By:	CEA
Revised:	---------	Aprv'd By:	CEA
Scale:	As Shown	FIGURE B.6	

Dissolved Phase Experiment
Methane and Acetate
August 5, 2002 (Day 193)
SERDP Hydrogen Biosparging Project

GSI Job No. G-2535
Issued: October 7, 2003

GROUNDWATER
SERVICES, INC.

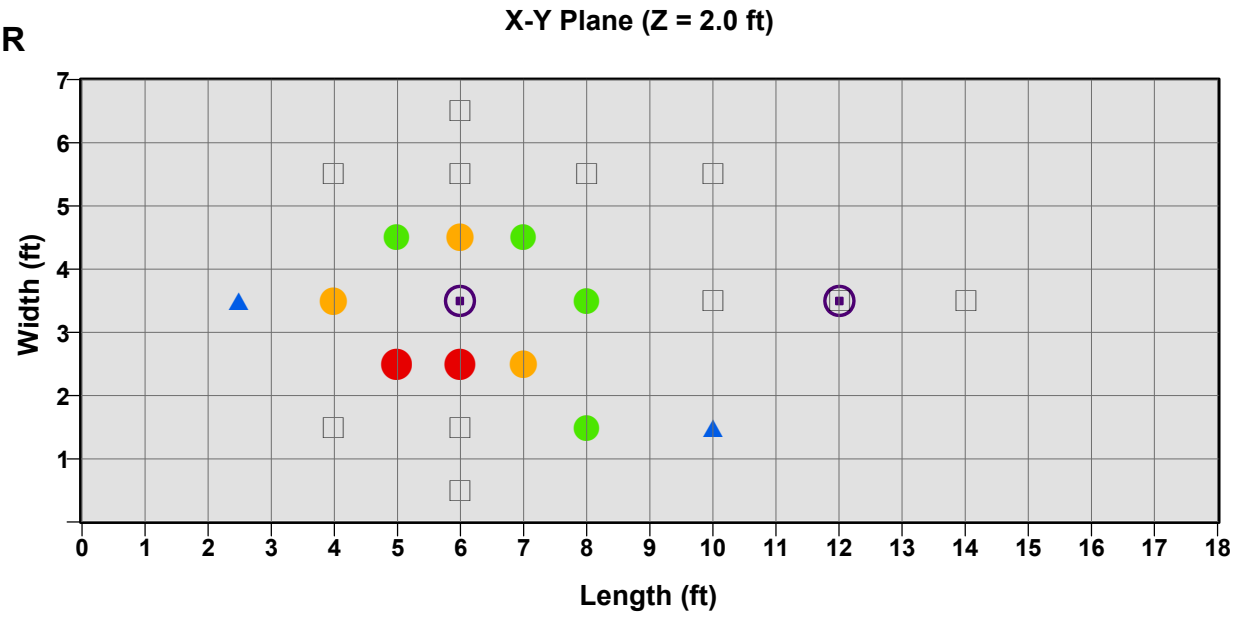
FINAL REPORT FOR LOW-VOLUME PULSED BIOSPARGING OF HYDROGEN FOR BIOREMEDIATION OF CHLORINATED SOLVENT PLUMES

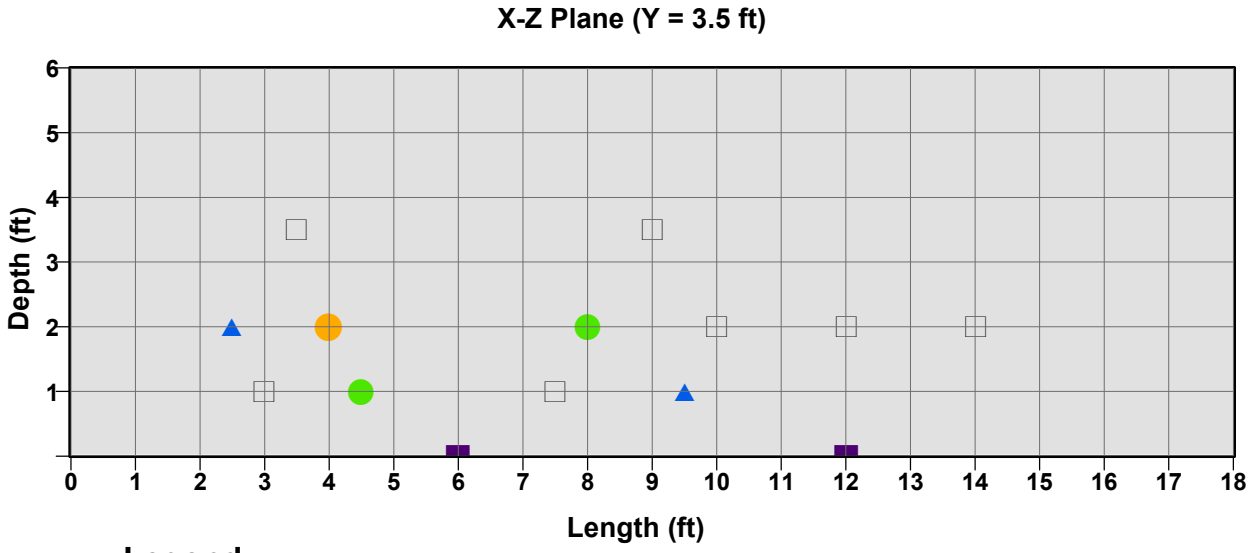
Groundwater Services, Inc., Houston, TX

APPENDIX C:

% Change in Gas Saturation Over Time in the ECRS Tank Using TDR

TDR





Legend

Gas Saturation

- < 0%
- >= 0 - 0.6%
- > 0.6 - 2.0 %
- > 2.0 - 5.0%
- > 5.0 %

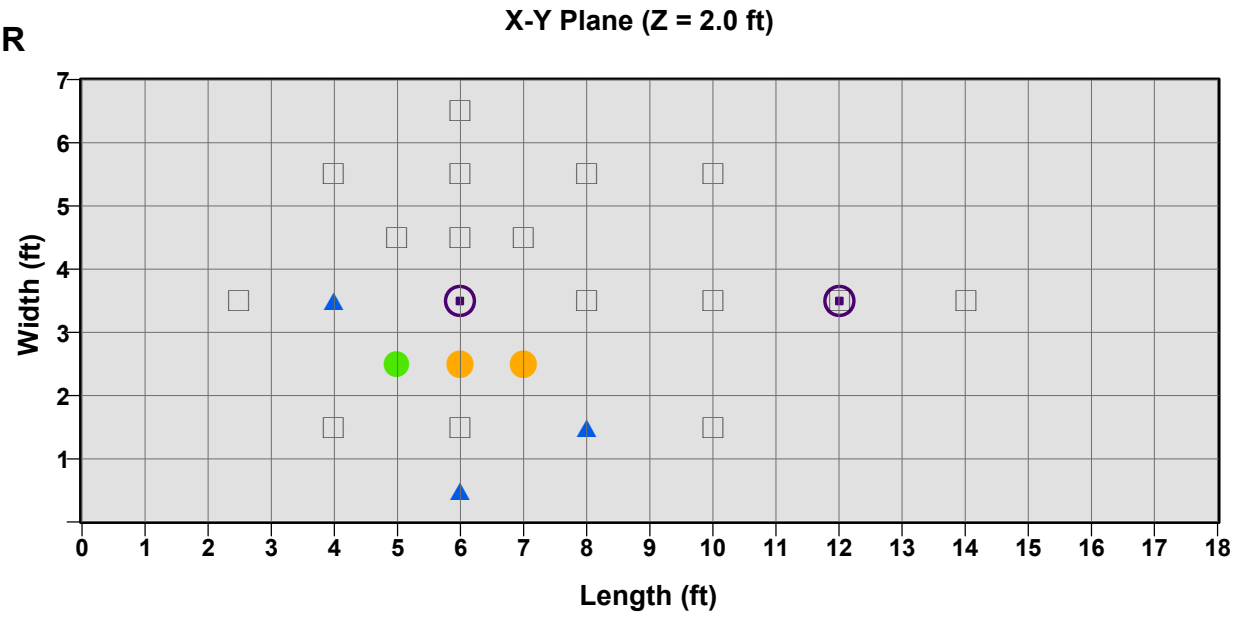
- Sparge Point in X-Y Plane
- Sparge Point in X-Z Plane

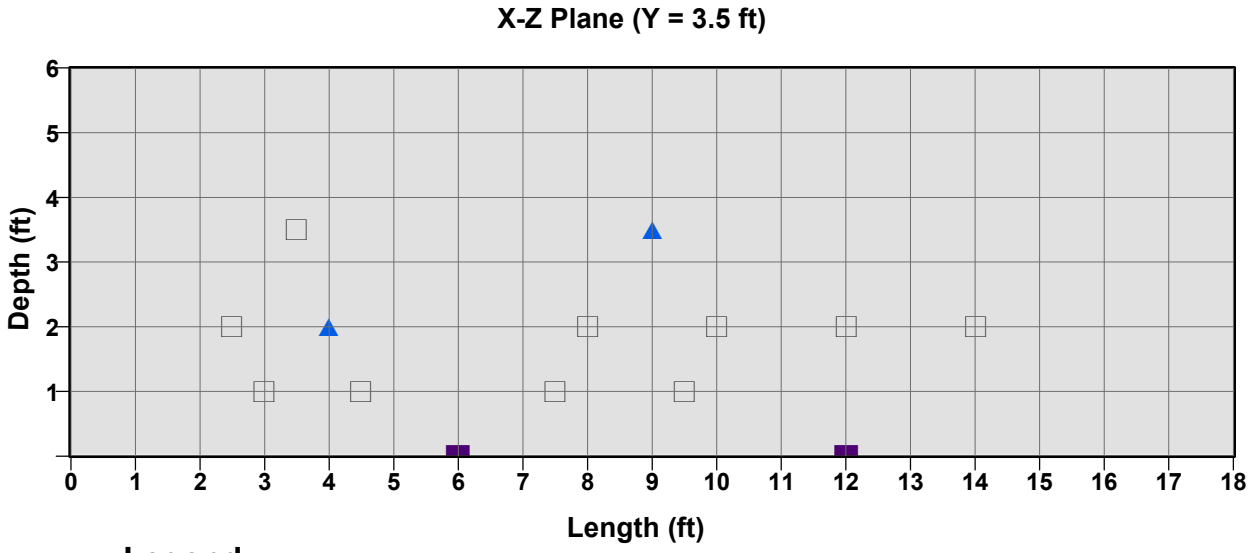
GROUNDWATER SERVICES, INC.

GSI Job No.	G-2535-107	Drawn By:	JJA
Issued:	7/16/03	Chk'd By:	CEA
Revised:	---------	Aprv'd By:	CEA
Scale:	As Shown	FIGURE C.1	

DISSOLVED PHASE EXPERIMENT
% Increase in Gas Saturation Using Time Domain Reflectometry (TDR)
February 18, 2002
(Before Bioaugmentation)
SERDP Hydrogen Biosparging Project

TDR





Legend

Gas Saturation

- < 0%
- >= 0 - 0.6%
- > 0.6 - 2.0 %
- > 2.0 - 5.0%
- > 5.0 %

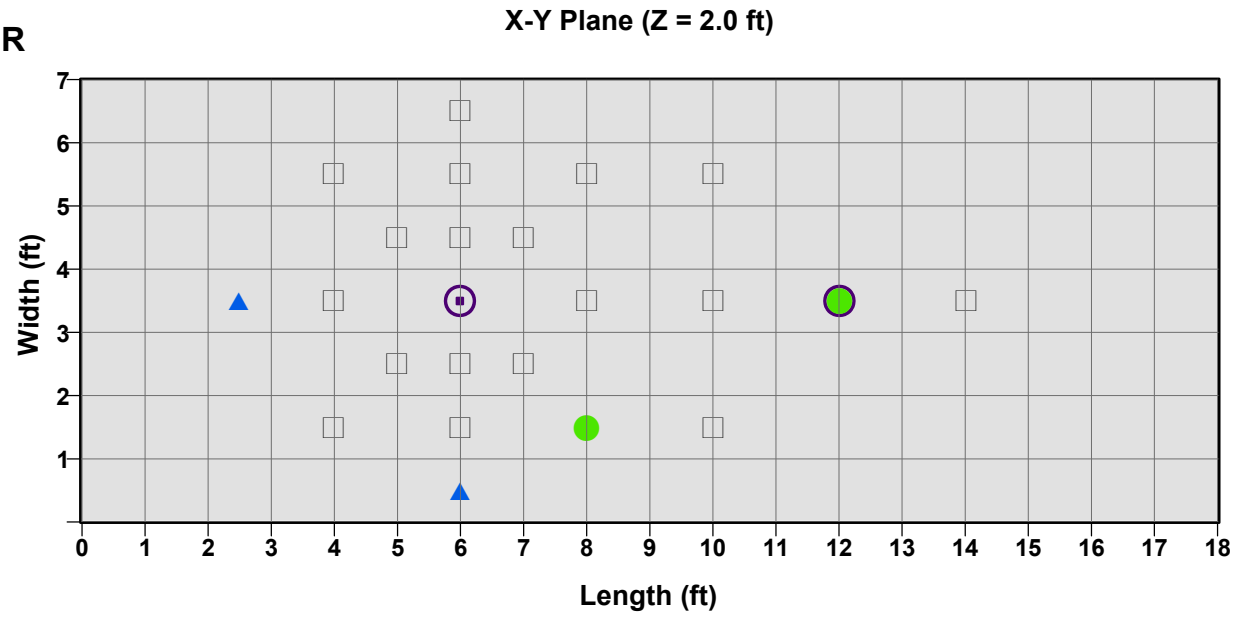
- Sparge Point in X-Y Plane
- Sparge Point in X-Z Plane

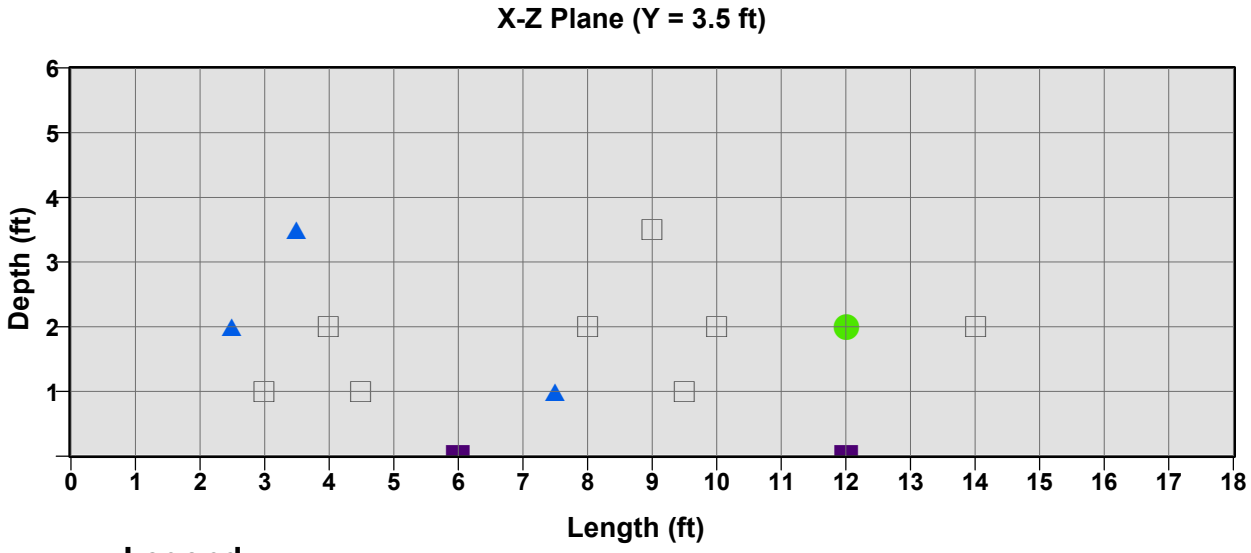
GROUNDWATER SERVICES, INC.

GSI Job No.	G-2535-107	Drawn By:	JJA
Issued:	7/16/03	Chk'd By:	CEA
Revised:	---------	Aprv'd By:	CEA
Scale:	As Shown	FIGURE C.2	

DISSOLVED PHASE EXPERIMENT
% Increase in Gas Saturation Using Time Domain Reflectometry (TDR)
April 12, 2002 (Day 81)
SERDP Hydrogen Biosparging Project

TDR





Legend

Gas Saturation

- < 0%
- >= 0 - 0.6%
- > 0.6 - 2.0 %
- > 2.0 - 5.0%
- > 5.0 %

- Sparge Point in X-Y Plane
- Sparge Point in X-Z Plane

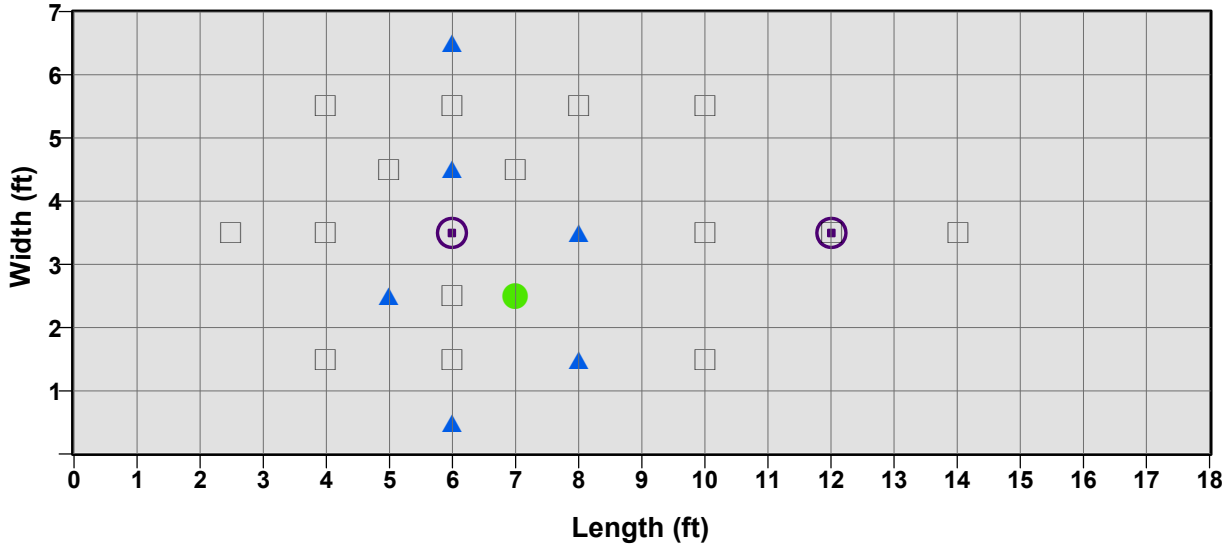
GROUNDWATER SERVICES, INC.

GSI Job No.	G-2535-107	Drawn By:	JJA
Issued:	7/16/03	Chk'd By:	CEA
Revised:	---------	Aprv'd By:	CEA
Scale:	As Shown	FIGURE C.3	

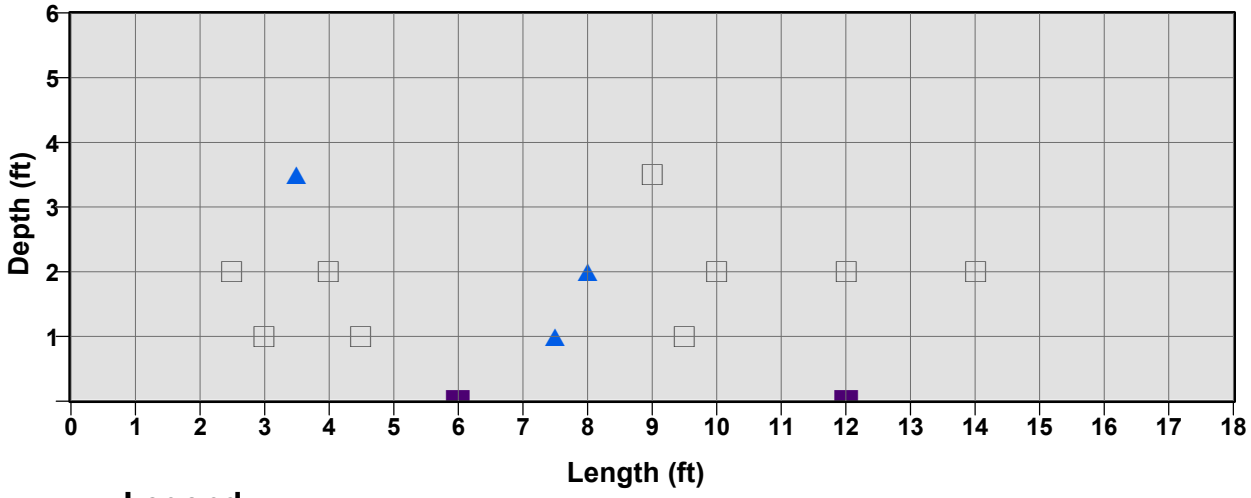
DISSOLVED PHASE EXPERIMENT
% Increase in Gas Saturation Using Time Domain Reflectometry (TDR)
May 16, 2002 (Day 115)
SERDP Hydrogen Biosparging Project

TDR

X-Y Plane (Z = 2.0 ft)



X-Z Plane (Y = 3.5 ft)



Legend

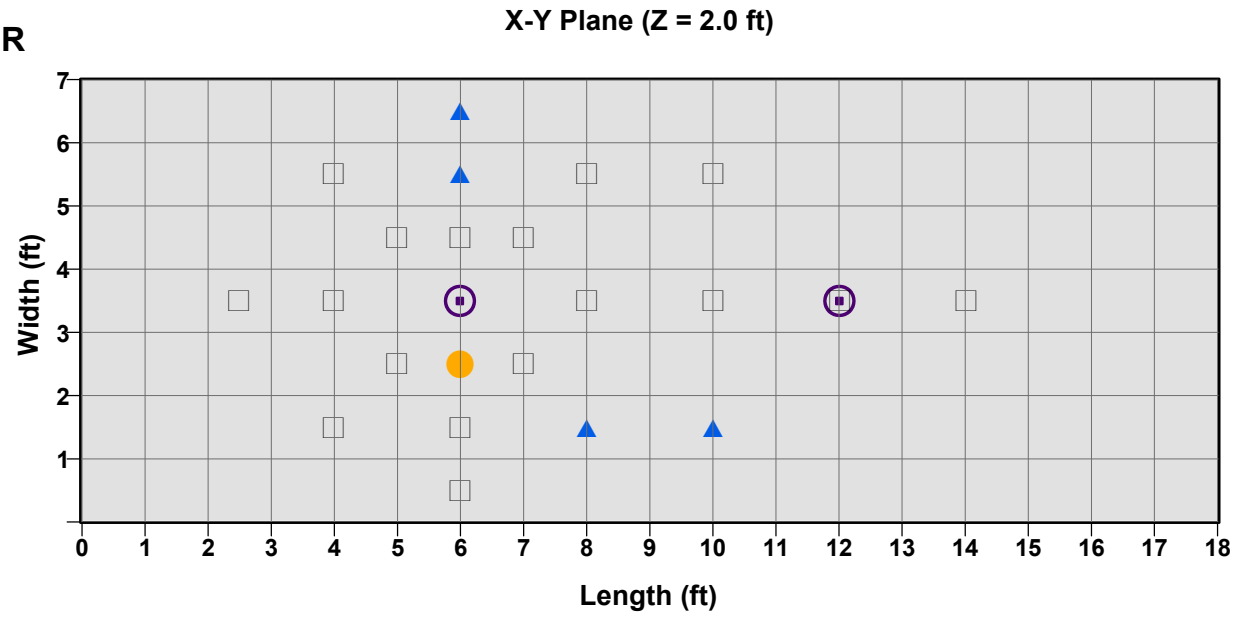
Gas Saturation

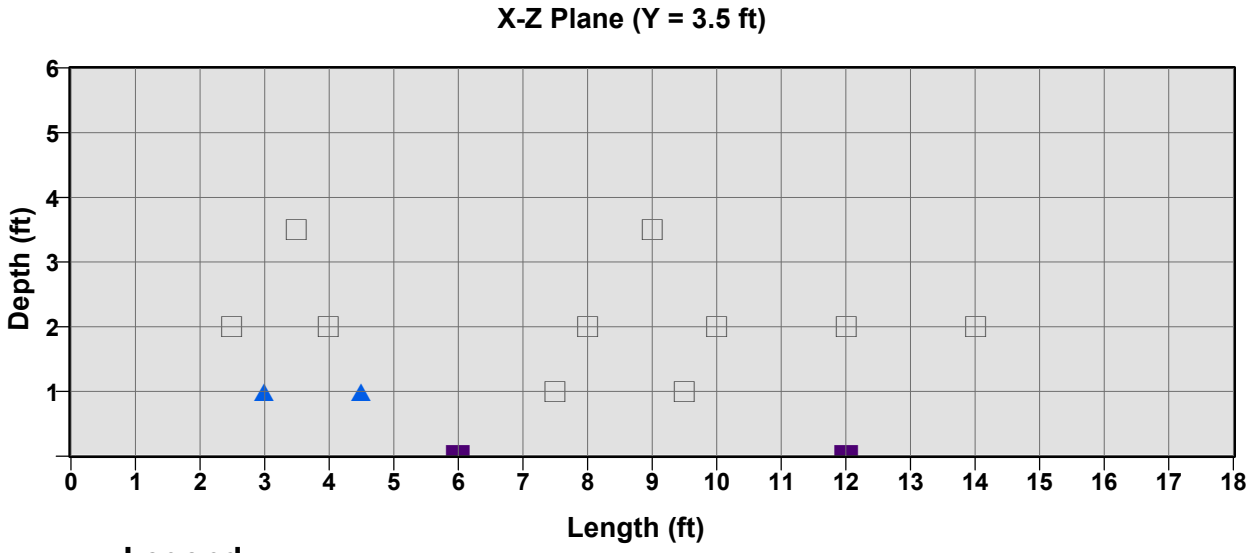
- < 0%
- >= 0 - 0.6%
- > 0.6 - 2.0 %
- > 2.0 - 5.0%
- > 5.0 %

- Sparge Point in X-Y Plane
- Sparge Point in X-Z Plane

GROUNDWATER SERVICES, INC.	GSI Job No. G-2535-107	Drawn By: JJA	DISSOLVED PHASE EXPERIMENT % Increase in Gas Saturation Using Time Domain Reflectometry (TDR) May 27, 2002 (Day 126) SERDP Hydrogen Biosparging Project
	Issued: 7/16/03	Chk'd By: CEA	
	Revised: ---------	Aprv'd By: CEA	
	Scale: As Shown	FIGURE C.4	

TDR





Legend

Gas Saturation

- < 0%
- >= 0 - 0.6%
- > 0.6 - 2.0 %
- > 2.0 - 5.0%
- > 5.0 %

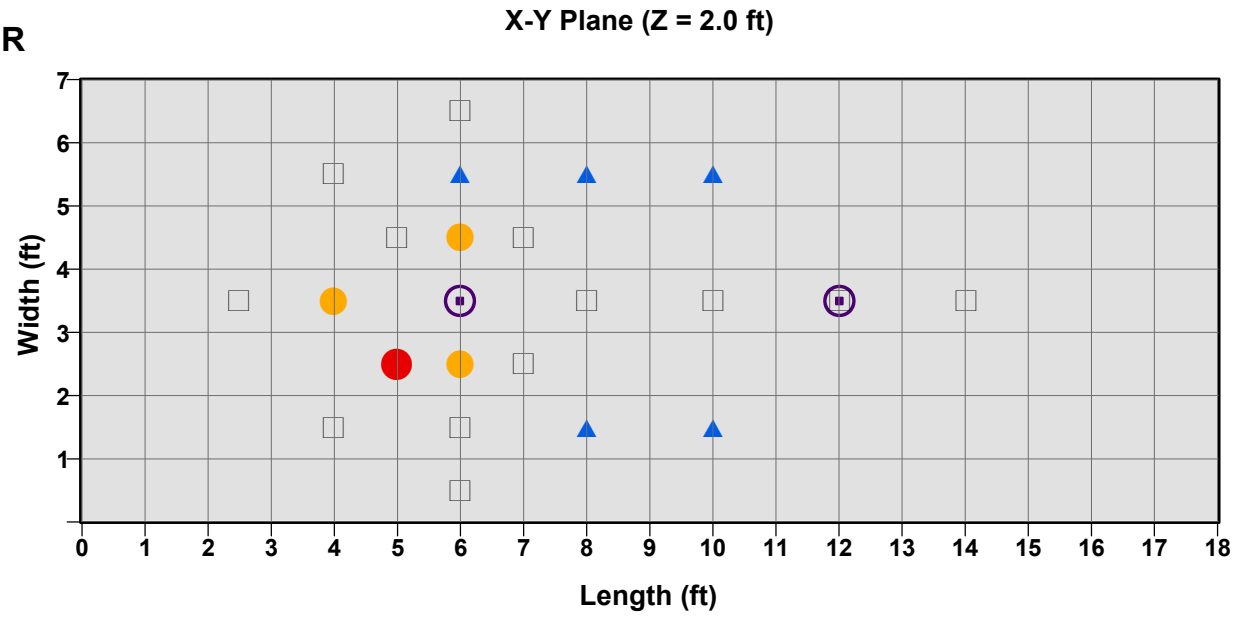
- Sparge Point in X-Y Plane
- Sparge Point in X-Z Plane

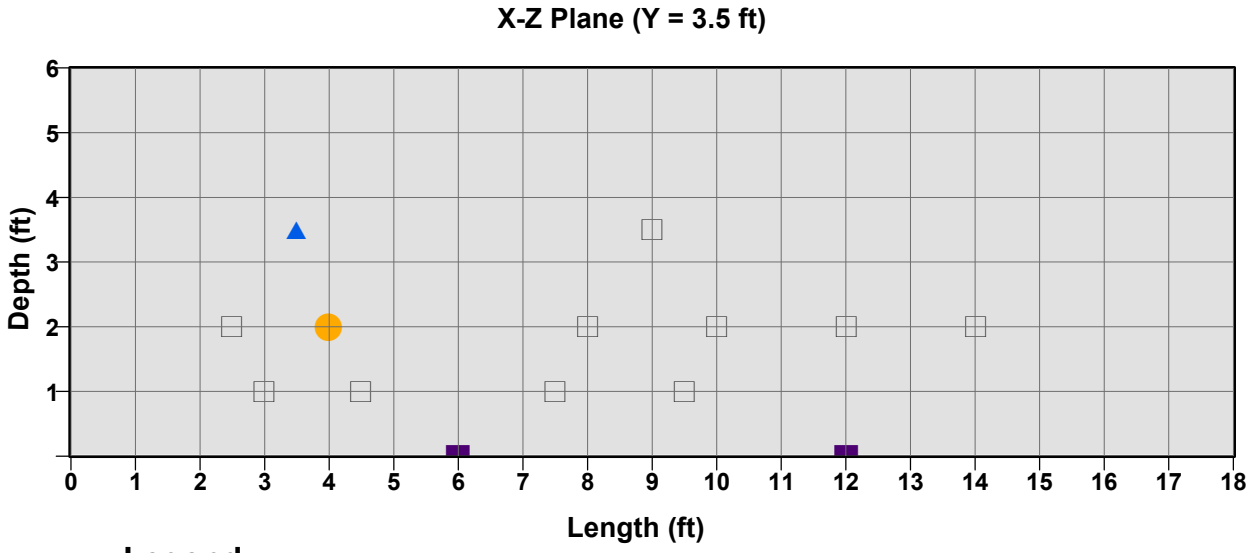
GROUNDWATER SERVICES, INC.

GSI Job No.	G-2535-107	Drawn By:	JJA
Issued:	7/16/03	Chk'd By:	CEA
Revised:	---------	Aprv'd By:	CEA
Scale:	As Shown	FIGURE C.5	

DISSOLVED PHASE EXPERIMENT
% Increase in Gas Saturation Using Time Domain Reflectometry (TDR)
July 17, 2002 (Day 177)
SERDP Hydrogen Biosparging Project

TDR





Legend

Gas Saturation

- < 0%
- >= 0 - 0.6%
- > 0.6 - 2.0 %
- > 2.0 - 5.0%
- > 5.0 %

- Sparge Point in X-Y Plane
- Sparge Point in X-Z Plane

GROUNDWATER SERVICES, INC.

GSI Job No.	G-2535-107	Drawn By:	JJA
Issued:	7/16/03	Chk'd By:	CEA
Revised:	---------	Aprv'd By:	CEA
Scale:	As Shown	FIGURE C.6	

DISSOLVED PHASE EXPERIMENT
% Increase in Gas Saturation Using Time Domain Reflectometry (TDR)
August 6, 2002 (Day 194)
SERDP Hydrogen Biosparging Project

GSI Job No. G-2535
Issued: October 7, 2003

GROUNDWATER
SERVICES, INC.

FINAL REPORT FOR LOW-VOLUME PULSED BIOSPARGING OF HYDROGEN FOR BIOREMEDIATION OF CHLORINATED SOLVENT PLUMES

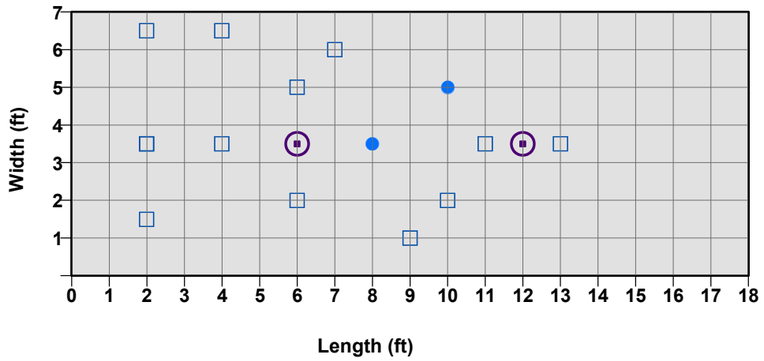
Groundwater Services, Inc., Houston, TX

APPENDIX D:

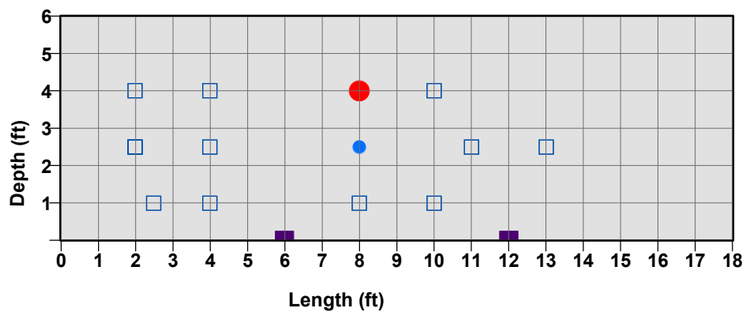
Data from Hydrogen Lifetime Experiments 1 and 2

X-Y Plane (Z = 2.5 ft)

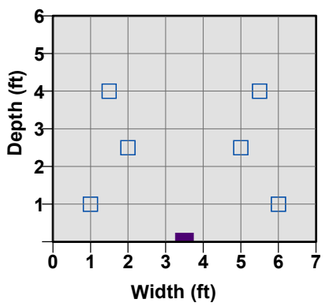
H_2



X-Z Plane (Y = 3.5 ft)



Z-Y Plane (X = 6 ft)



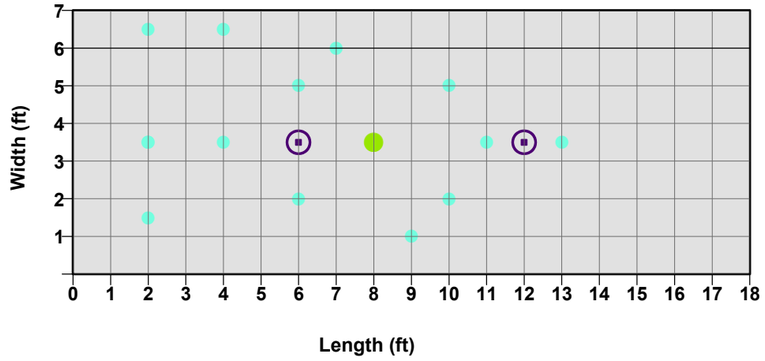
Legend

H_2 Concentration

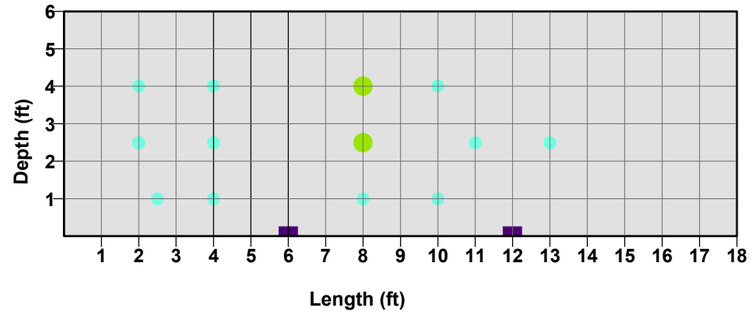
- < 1.0 ug/L
- > 1.0 - 5.0 ug/L
- > 5.0 - 25.0 ug/L
- > 25.0 ug/L
- Sparge Point X-Z Plane
- Sparge Point X-Y Plane

X-Y Plane (Z = 2.5 ft)

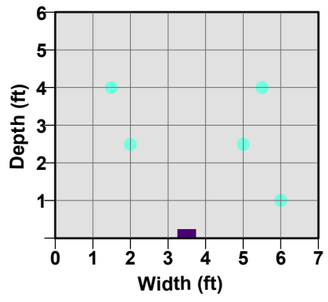
SF_6



X-Z Plane (Y = 3.5 ft)



Z-Y Plane (X = 6 ft)



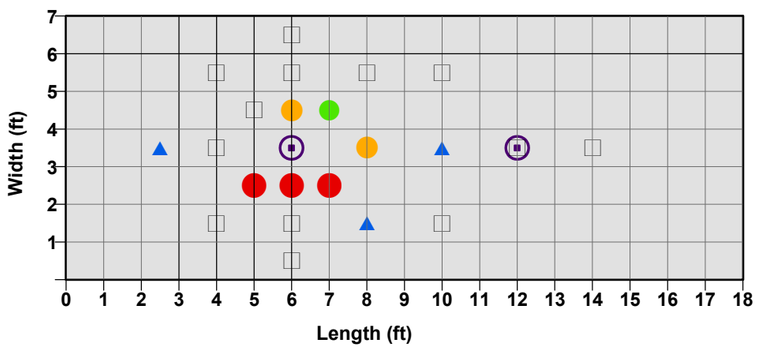
Legend

SF_6 Concentration

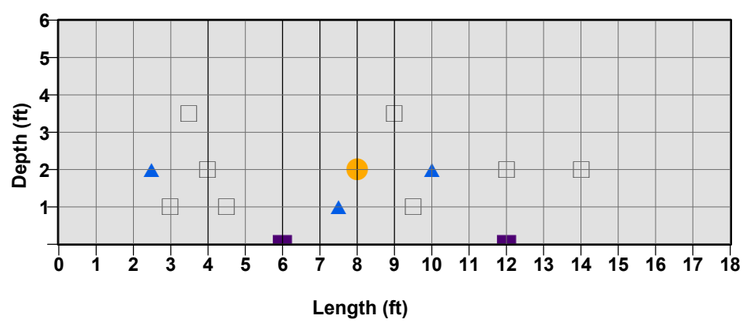
- 0 - 0.5 ug/L
- > 0.5 - 1.0 ug/L
- > 1.0 - 5.0 ug/L
- > 5.0 - 20.0 ug/L
- > 20.0 ug/L
- Sparge Point Y-Z Plane
- Sparge Point X-Y Plane

X-Y Plane (Z = 2.0 ft)

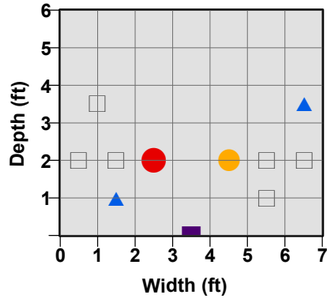
TDR



X-Z Plane (Y = 3.5 ft)



Z-Y Plane (X = 6 ft)



Legend

Gas Saturation

- < 0%
- >= 0 - 0.6%
- > 0.6 - 2.0 %
- > 2.0 - 5.0%
- > 5.0 %
- Sparge Point Y-Z Plane
- Sparge Point X-Y Plane

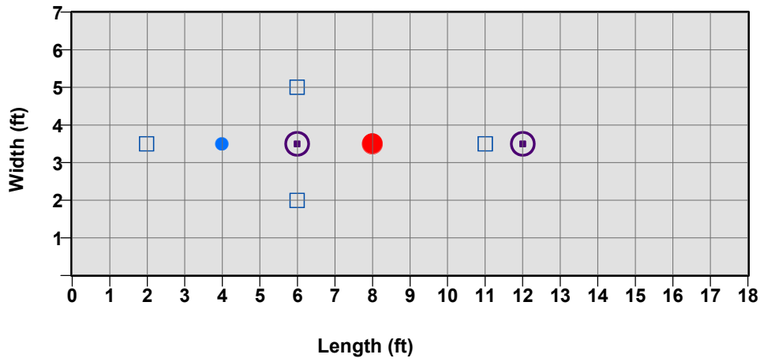
GROUNDWATER SERVICES, INC.

GSI Job No.	G-2535-107	Drawn By:	JJA
Issued:	7/16/03	Chk'd By:	CEA
Revised:	---------	Aprv'd By:	CEA
Scale:	As Shown	FIGURE D.1	

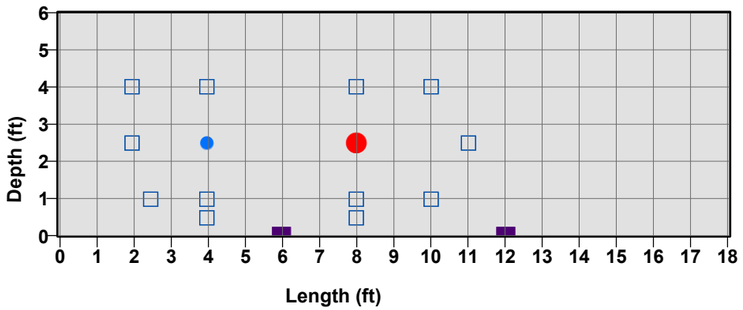
DISSOLVED PHASE EXPERIMENT
Hydrogen Lifetime Experiment 1
March 24, 2002 (1 hour after sparge)
SERDP Hydrogen Biosparging Project

X-Y Plane (Z = 2.5 ft)

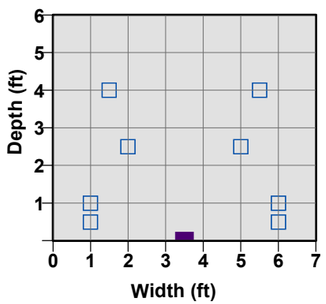
H_2



X-Z Plane (Y = 3.5 ft)



Z-Y Plane (X = 6 ft)



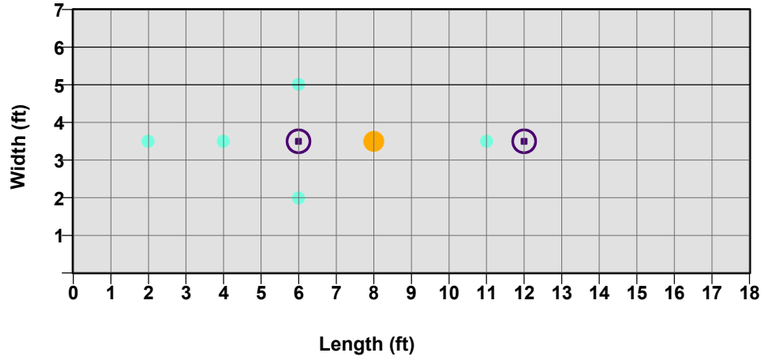
Legend

H_2 Concentration

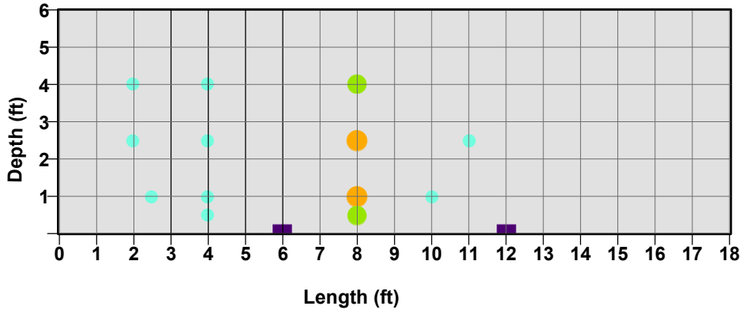
- < 1.0 ug/L
- > 1.0 - 5.0 ug/L
- > 5.0 - 25.0 ug/L
- > 25.0 ug/L
- Sparge Point X-Z Plane
- Sparge Point X-Y Plane

X-Y Plane (Z = 2.5 ft)

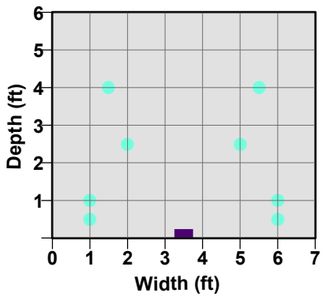
SF_6



X-Z Plane (Y = 3.5 ft)



Z-Y Plane (X = 6 ft)



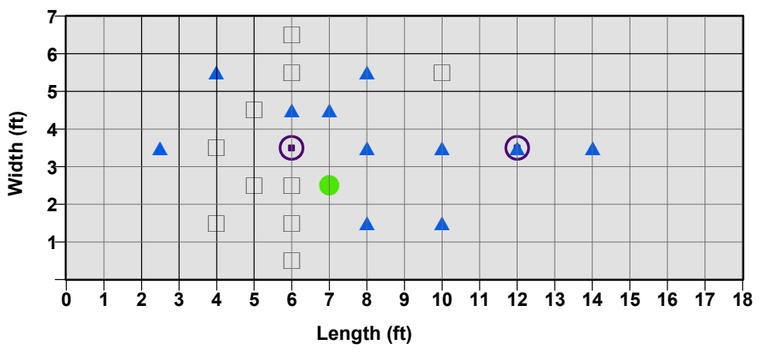
Legend

SF_6 Concentration

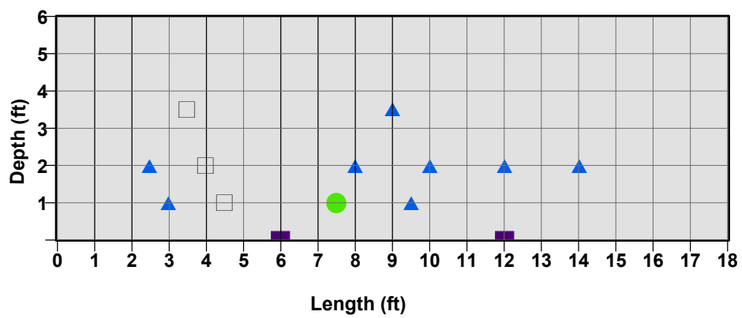
- 0 - 0.5 ug/L
- > 0.5 - 1.0 ug/L
- > 1.0 - 5.0 ug/L
- > 5.0 - 20.0 ug/L
- > 20.0 ug/L
- Sparge Point Y-Z Plane
- Sparge Point X-Y Plane

X-Y Plane (Z = 2.0 ft)

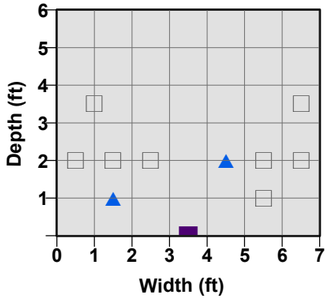
TDR



X-Z Plane (Y = 3.5 ft)



Z-Y Plane (X = 6 ft)



Legend

Gas Saturation

- < 0%
- >= 0 - 0.6%
- > 0.6 - 2.0 %
- > 2.0 - 5.0%
- > 5.0 %
- Sparge Point Y-Z Plane
- Sparge Point X-Y Plane

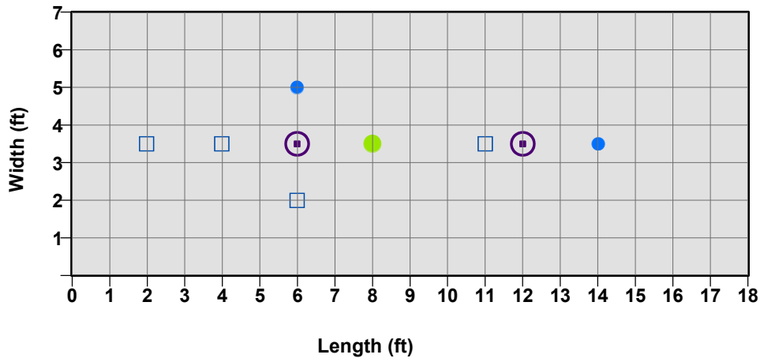
GROUNDWATER SERVICES, INC.

GSI Job No.	G-2535-107	Drawn By:	JJA
Issued:	7/16/03	Chk'd By:	CEA
Revised:	---------	Aprv'd By:	CEA
Scale:	As Shown	FIGURE D.2	

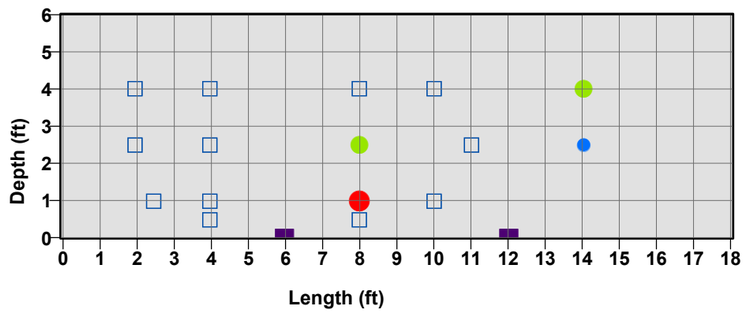
DISSOLVED PHASE EXPERIMENT
Hydrogen Lifetime Experiment 1
March 25, 2002 (24 hours after sparge)
SERDP Hydrogen Biosparging Project

X-Y Plane (Z = 2.5 ft)

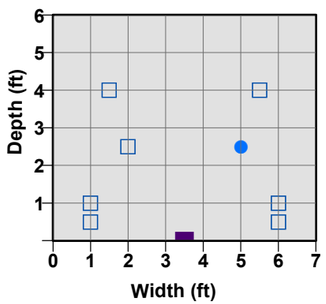
H_2



X-Z Plane (Y = 3.5 ft)



Z-Y Plane (X = 6 ft)



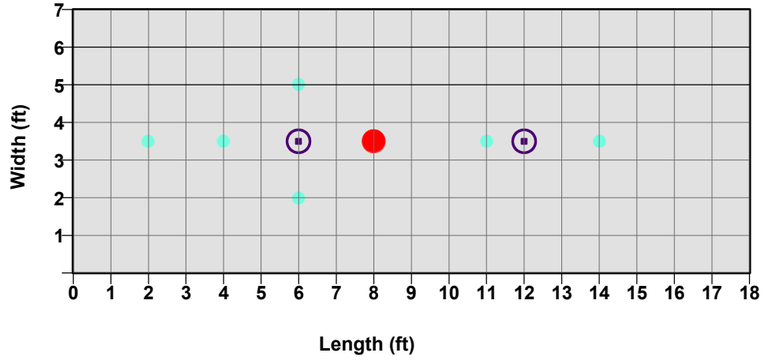
Legend

H_2 Concentration

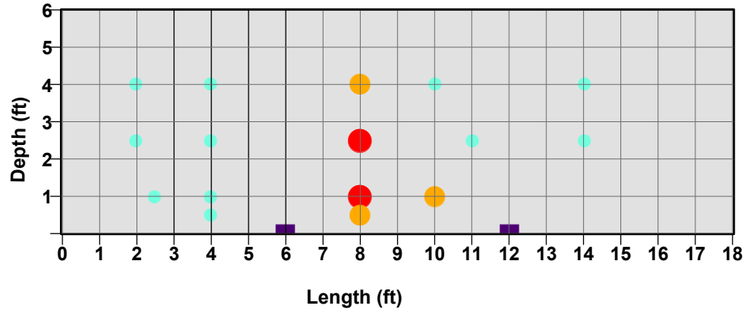
- < 1.0 ug/L
- > 1.0 - 5.0 ug/L
- > 5.0 - 25.0 ug/L
- > 25.0 ug/L
- Sparge Point X-Z Plane
- Sparge Point X-Y Plane

X-Y Plane (Z = 2.5 ft)

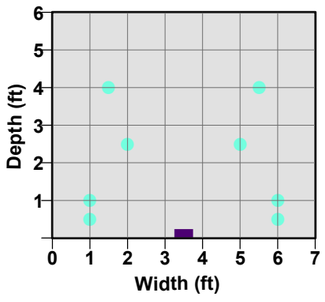
SF_6



X-Z Plane (Y = 3.5 ft)



Z-Y Plane (X = 6 ft)



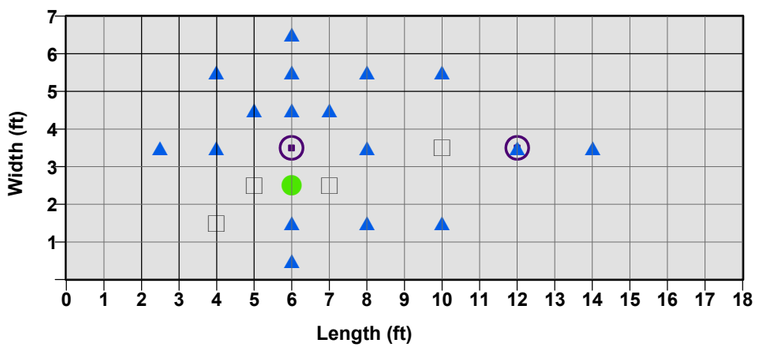
Legend

SF_6 Concentration

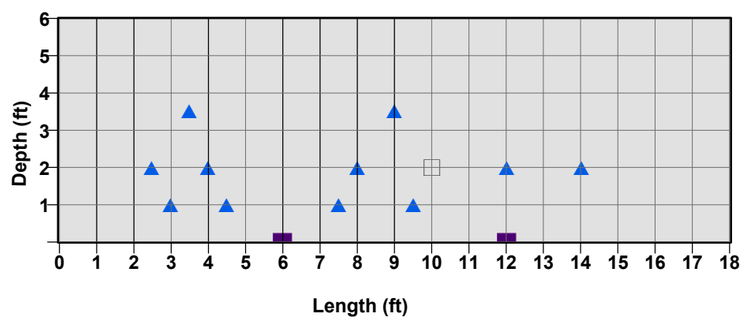
- 0 - 0.5 ug/L
- > 0.5 - 1.0 ug/L
- > 1.0 - 5.0 ug/L
- > 5.0 - 20.0 ug/L
- > 20.0 ug/L
- Sparge Point Y-Z Plane
- Sparge Point X-Y Plane

X-Y Plane (Z = 2.0 ft)

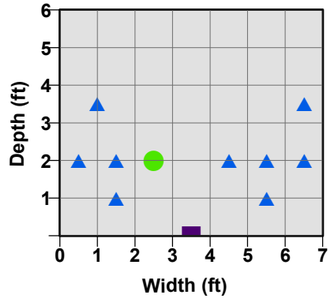
TDR



X-Z Plane (Y = 3.5 ft)



Z-Y Plane (X = 6 ft)



Legend

Gas Saturation

- < 0%
- >= 0 - 0.6%
- > 0.6 - 2.0 %
- > 2.0 - 5.0%
- > 5.0 %
- Sparge Point Y-Z Plane
- Sparge Point X-Y Plane

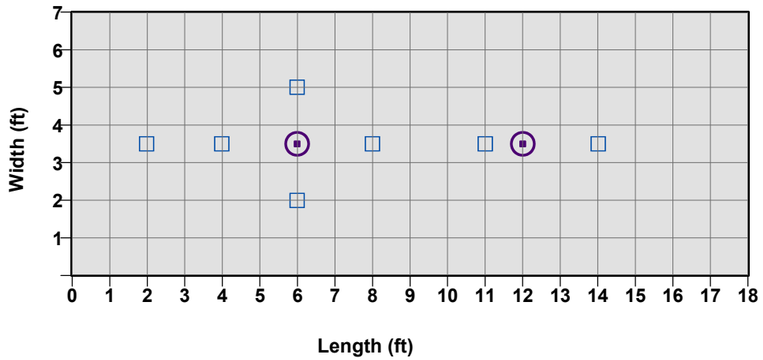
GROUNDWATER SERVICES, INC.

GSI Job No.	G-2535-107	Drawn By:	JJA
Issued:	7/16/03	Chk'd By:	CEA
Revised:	---------	Aprv'd By:	CEA
Scale:	As Shown	FIGURE D.3	

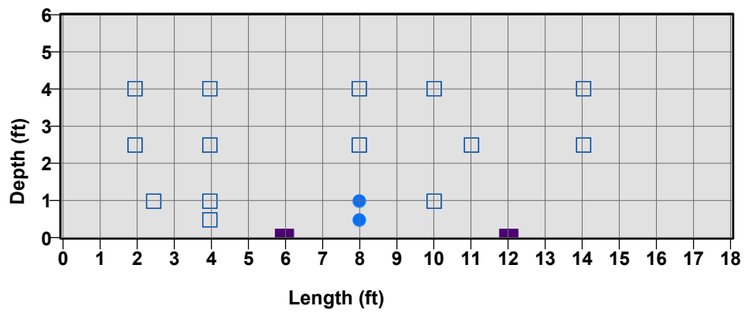
DISSOLVED PHASE EXPERIMENT
Hydrogen Lifetime Experiment 1
March 26, 2002 (48 hours after sparge)
SERDP Hydrogen Biosparging Project

X-Y Plane (Z = 2.5 ft)

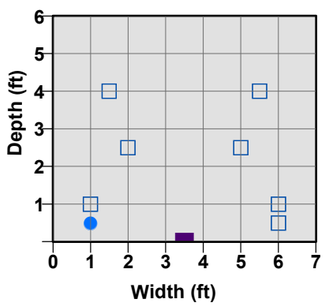
H_2



X-Z Plane (Y = 3.5 ft)



Z-Y Plane (X = 6 ft)



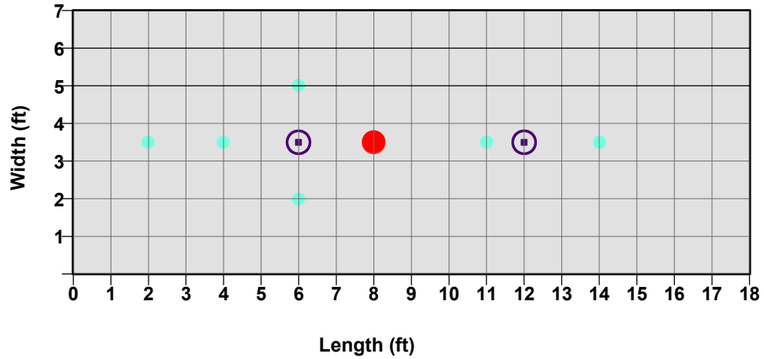
Legend

H_2 Concentration

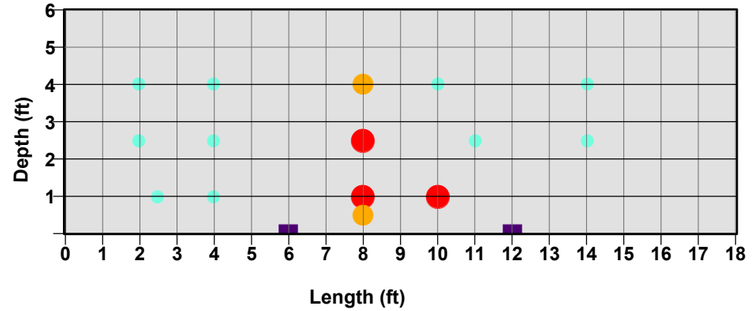
- < 1.0 ug/L
- > 1.0 - 5.0 ug/L
- > 5.0 - 25.0 ug/L
- > 25.0 ug/L
- Sparge Point X-Z Plane
- Sparge Point X-Y Plane

X-Y Plane (Z = 2.5 ft)

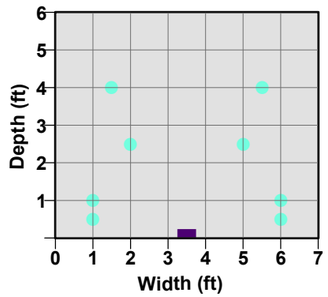
SF_6



X-Z Plane (Y = 3.5 ft)



Z-Y Plane (X = 6 ft)



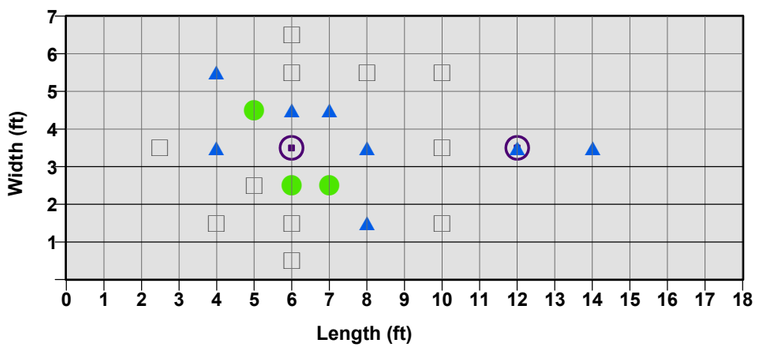
Legend

SF_6 Concentration

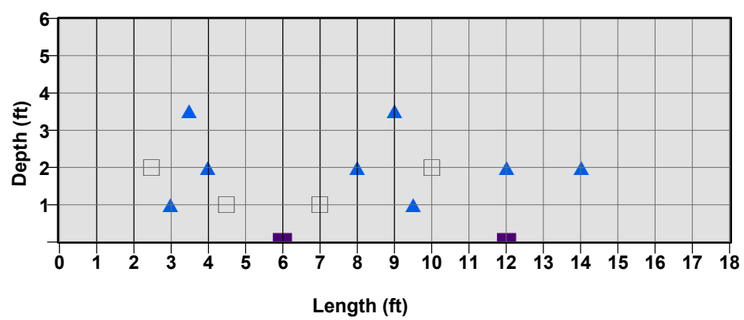
- 0 - 0.5 ug/L
- > 0.5 - 1.0 ug/L
- > 1.0 - 5.0 ug/L
- > 5.0 - 20.0 ug/L
- > 20.0 ug/L
- Sparge Point Y-Z Plane
- Sparge Point X-Y Plane

X-Y Plane (Z = 2.0 ft)

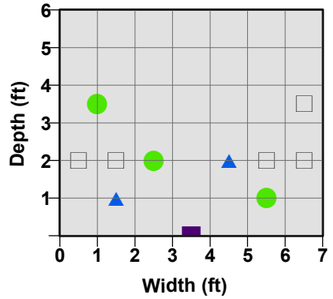
TDR



X-Z Plane (Y = 3.5 ft)



Z-Y Plane (X = 6 ft)



Legend

Gas Saturation

- < 0%
- >= 0 - 0.6%
- > 0.6 - 2.0 %
- > 2.0 - 5.0%
- > 5.0 %
- Sparge Point Y-Z Plane
- Sparge Point X-Y Plane

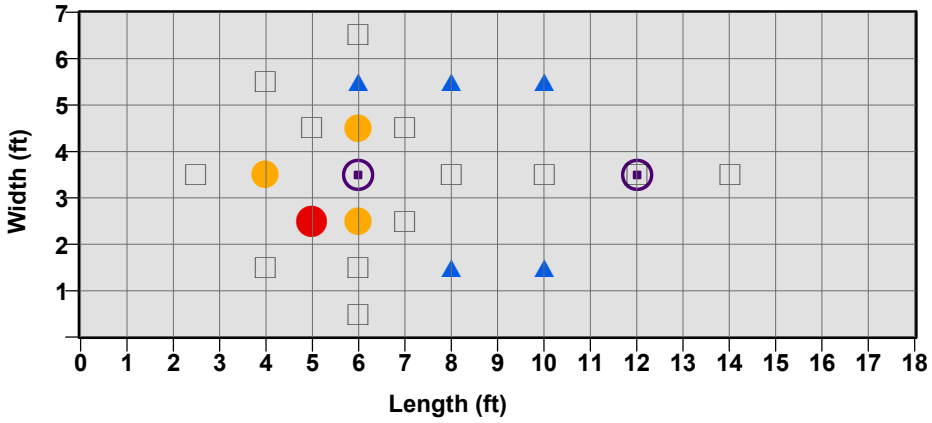
GROUNDWATER SERVICES, INC.

GSI Job No.	G-2535-107	Drawn By:	JJA
Issued:	7/16/03	Chk'd By:	CEA
Revised:	---------	Aprv'd By:	CEA
Scale:	As Shown	FIGURE D.4	

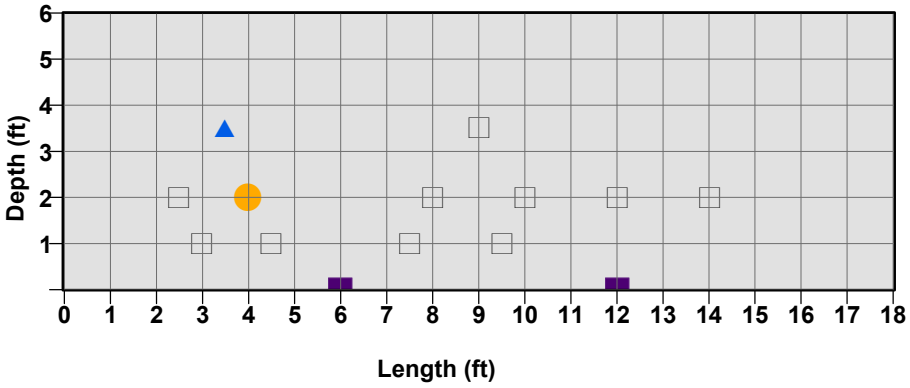
DISSOLVED PHASE EXPERIMENT
Hydrogen Lifetime Experiment 1
March 28, 2002 (96 hours after sparge)
SERDP Hydrogen Biosparging Project

X-Y Plane (Z = 2.0 ft)

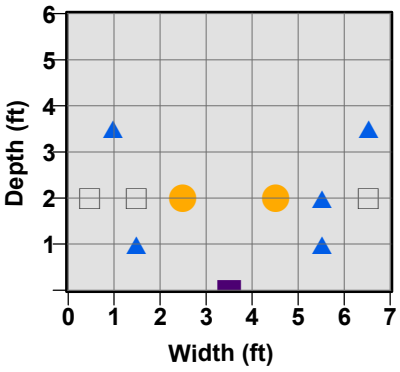
TDR



X-Z Plane (Y = 3.5 ft)



Z-Y Plane (X = 6 ft)



Legend

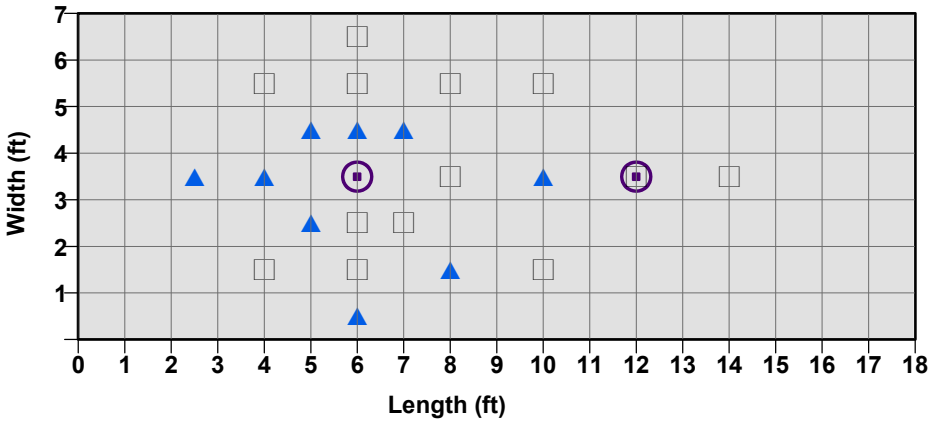
Gas Saturation

- < 0%
- >= 0 - 0.6%
- > 0.6 - 2.0 %
- > 2.0 - 5.0%
- > 5.0 %
- Sparge Point Y-Z Plane
- Sparge Point X-Y Plane

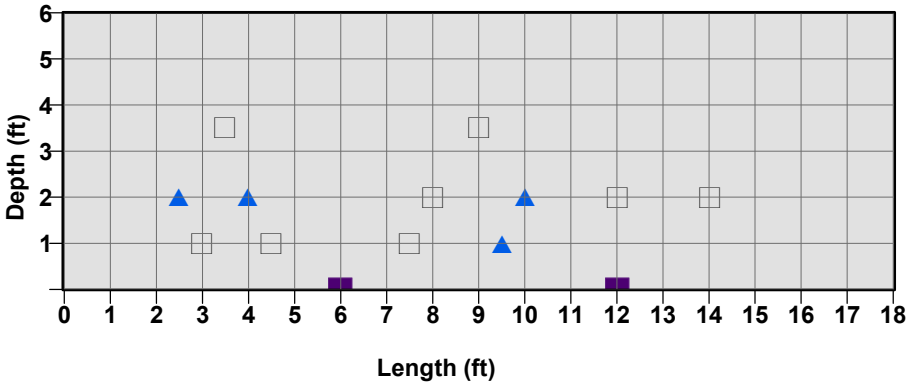
GROUNDWATER SERVICES, INC.	GSI Job No. G-2535-107	Drawn By: JJA	**DISSOLVED PHASE EXPERIMENT**
	Issued: 7/16/03	Chk'd By: CEA	**Hydrogen Lifetime Experiment 2**
	Revised: ---------	Aprv'd By: CEA	**August 6, 2002 (immediately after sparge)**
	Scale: As Shown	**FIGURE D.5**	**SERDP Hydrogen Biosparging Project**

X-Y Plane (Z = 2.0 ft)

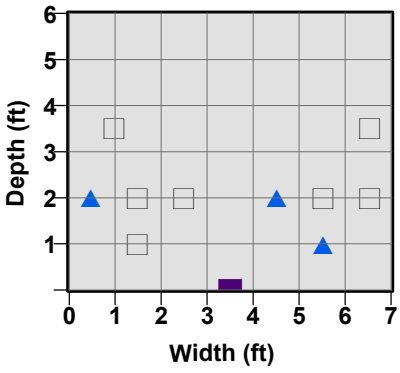
TDR



X-Z Plane (Y = 3.5 ft)



Z-Y Plane (X = 6 ft)



Legend

Gas Saturation

- < 0%
- >= 0 - 0.6%
- > 0.6 - 2.0 %
- > 2.0 - 5.0%
- > 5.0 %
- Sparge Point Y-Z Plane
- Sparge Point X-Y Plane

GROUNDWATER SERVICES, INC.	GSI Job No. G-2535-107	Drawn By: JJA	**DISSOLVED PHASE EXPERIMENT** **Hydrogen Lifetime Experiment 2** **August 7, 2002 (24 hours after sparge)** **SERDP Hydrogen Biosparging Project**
	Issued: 7/16/03	Chk'd By: CEA	
	Revised: ---------	Aprv'd By: CEA	
	Scale: As Shown	**FIGURE D.6**	

GSI Job No. G-2535
Issued: October 7, 2003

GROUNDWATER
SERVICES, INC.

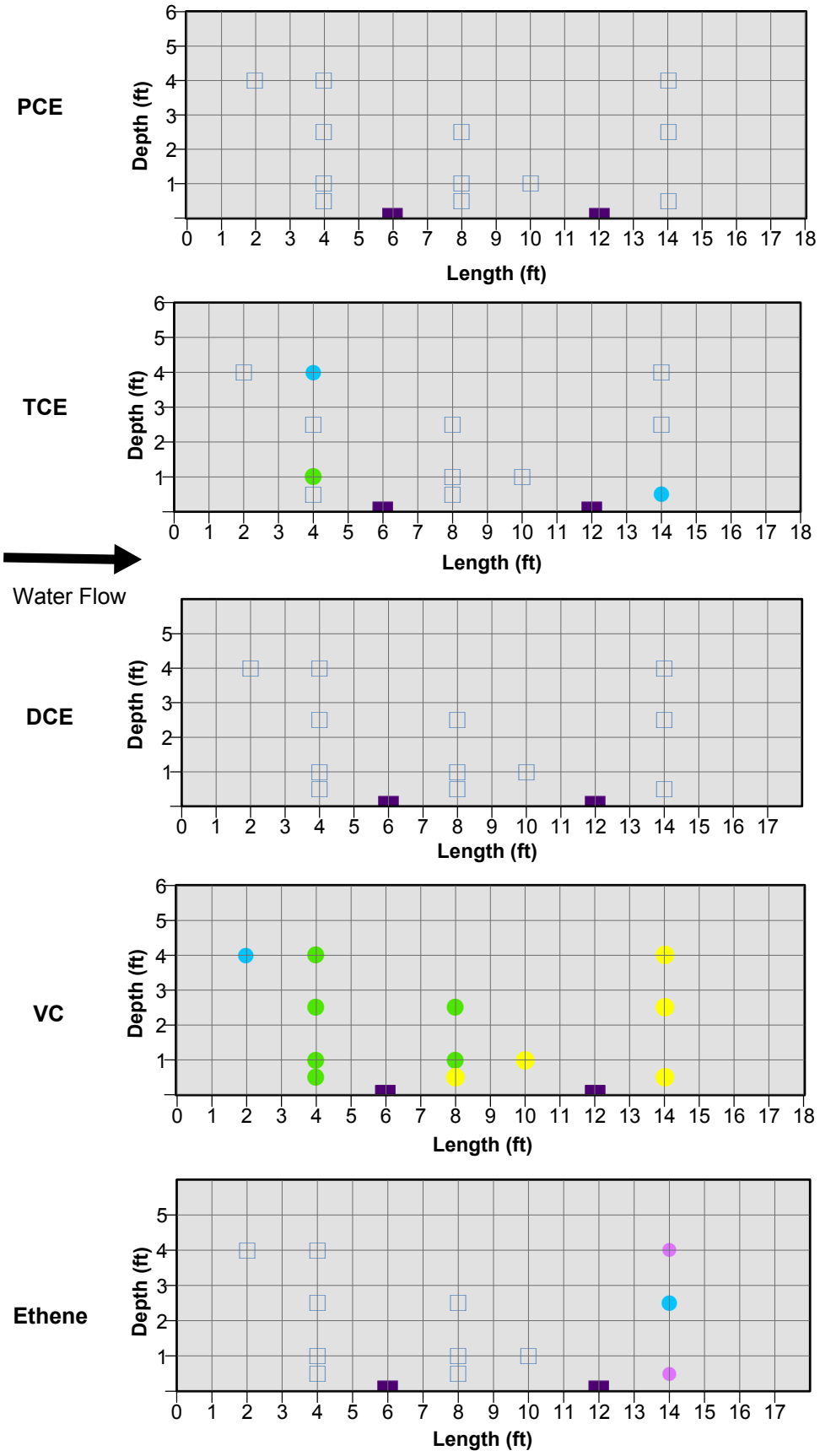
FINAL REPORT FOR LOW-VOLUME PULSED BIOSPARGING OF HYDROGEN FOR BIOREMEDIATION OF CHLORINATED SOLVENT PLUMES

Groundwater Services, Inc., Houston, TX

APPENDIX E:

Distribution of Chlorinated Ethenes and Ethene within the ECRS Tank
(DNAPL Experiment)

X-Z Plane (Y = 3.5 ft)



Legend

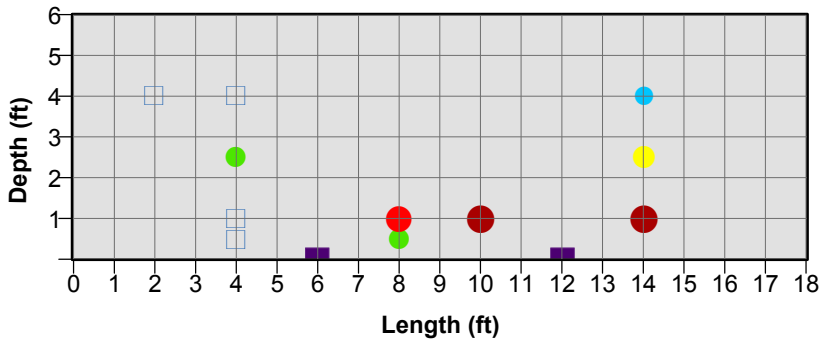
Concentration (uM)

- ND
- 0.001 - 0.1 uM
- >0.1 - 1.0 uM
- > 1 - 2 uM
- > 2 - 20 uM
- >20 - 100 uM
- > 100 - 300 uM
- > 300 - 1000 uM
- >1000 uM
- Sparge Point X-Z Plane

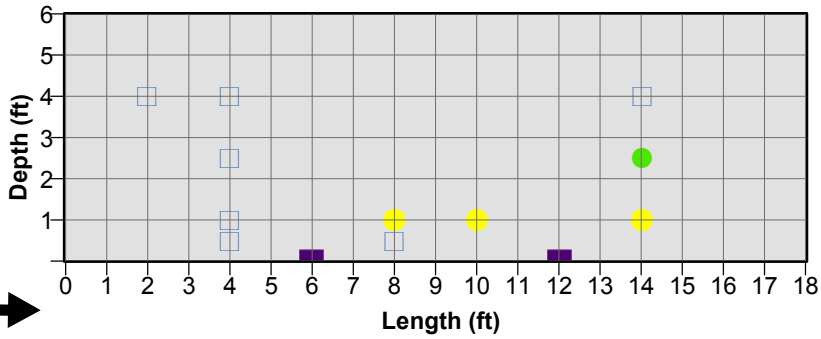
GROUNDWATER SERVICES, INC.	GSI Job No. G-2535-107	Drawn By: JJA	**DNAPL PHASE EXPERIMENT** **Chlorinated Ethenes + Ethene** **August 23, 2002** **(Before DNAPL Addition)** **SERDP Hydrogen Biosparging Project**
	Issued: 7/16/03	Chk'd By: CEA	
	Revised: ---------	Aprv'd By: CEA	
	Scale: As Shown	**FIGURE E.1**	

X-Z Plane (Y = 3.5 ft)

PCE

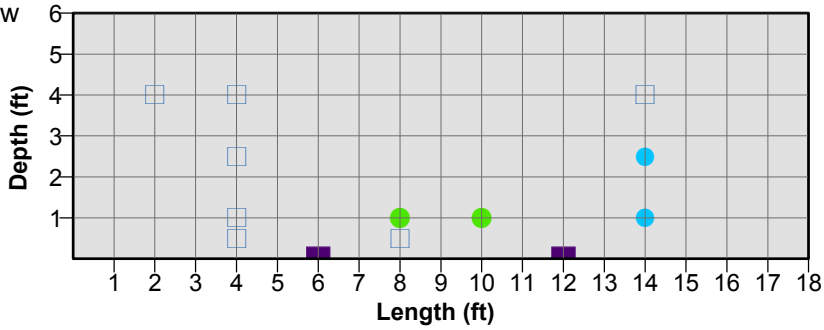


TCE

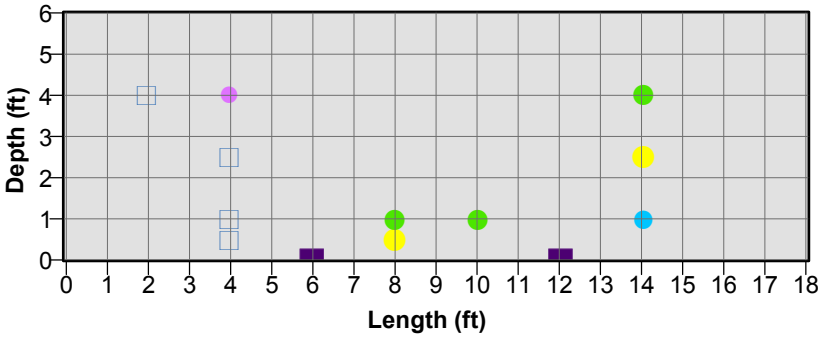


Water Flow

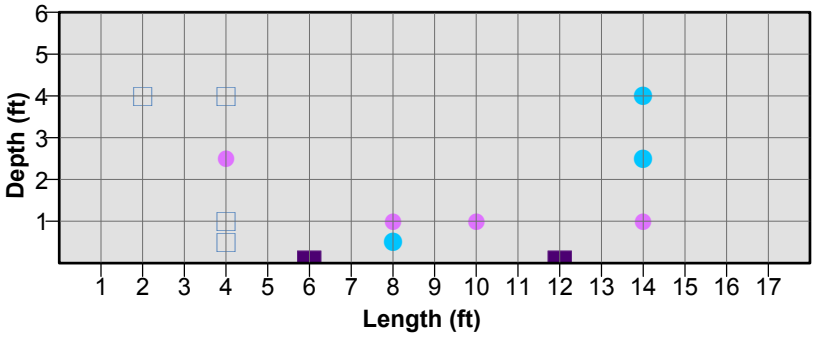
DCE



VC



Ethene



Legend

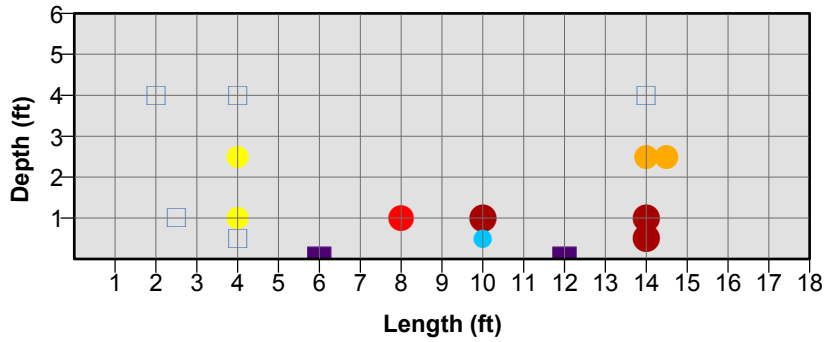
Concentration (uM)

- ND
- 0.001 - 0.1 uM
- >0.1 - 1.0 uM
- > 1 - 2 uM
- > 2 - 20 uM
- >20 - 100 uM
- > 100 - 300 uM
- > 300 - 1000 uM
- >1000 uM
- Sparge Point X-Z Plane

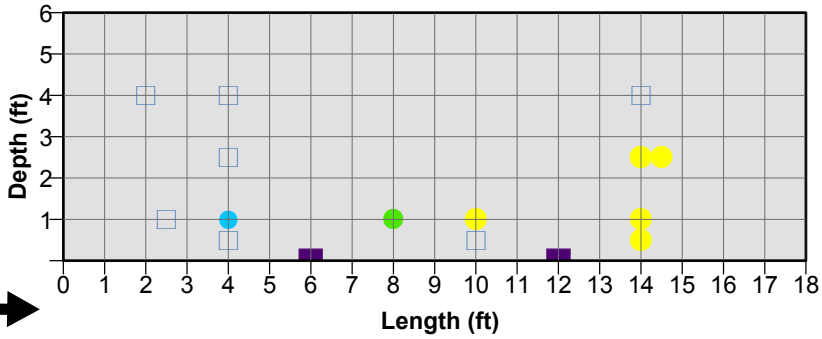
GROUNDWATER SERVICES, INC.	GSI Job No. G-2535-107	Drawn By: JJA	DNAPL PHASE EXPERIMENT Chlorinated Ethenes + Ethene September 9, 2002 (Day 17) SERDP Hydrogen Biosparging Project
	Issued: 7/16/03	Chk'd By: CEA	
	Revised: ---------	Aprv'd By: CEA	
	Scale: As Shown	FIGURE E.2	

X-Z Plane (Y = 3.5 ft)

PCE

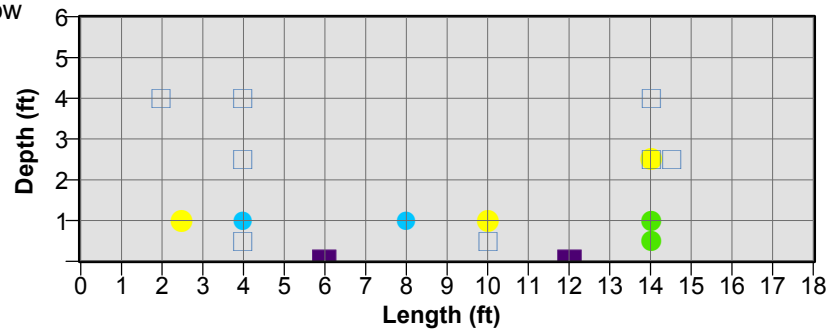


TCE

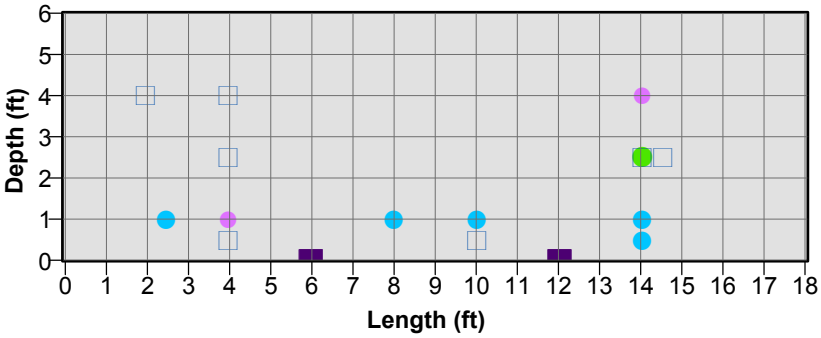


Water Flow

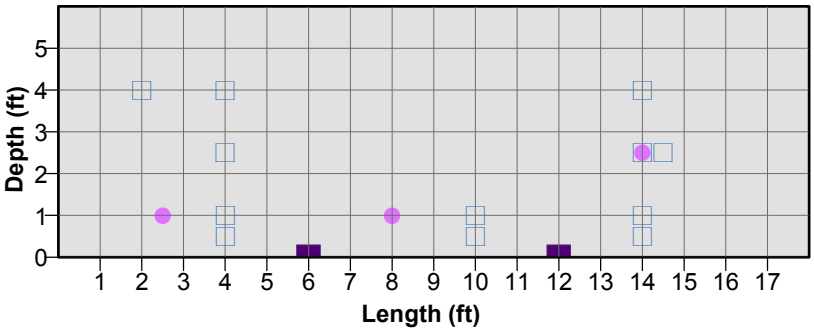
DCE



VC



Ethene



Legend

Concentration (uM)

- ND
- 0.001 - 0.1 uM
- >0.1 - 1.0 uM
- > 1 - 2 uM
- > 2 - 20 uM
- >20 - 100 uM
- > 100 - 300 uM
- > 300 - 1000 uM
- >1000 uM
- Sparge Point X-Z Plane

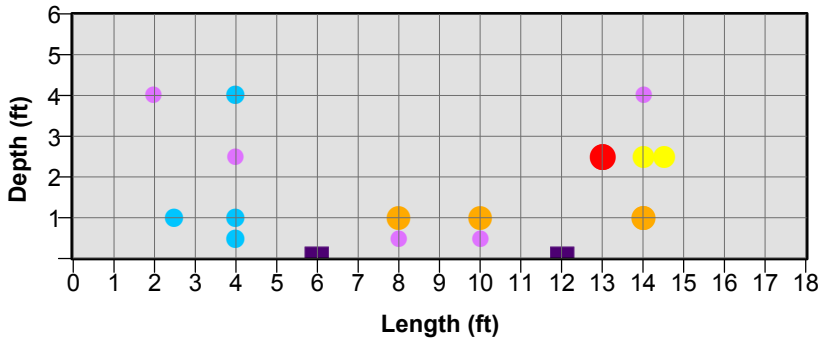
GROUNDWATER SERVICES, INC.

GSI Job No.	G-2535-107	Drawn By:	JJA
Issued:	7/16/03	Chk'd By:	CEA
Revised:	---------	Aprv'd By:	CEA
Scale:	As Shown	FIGURE E.3	

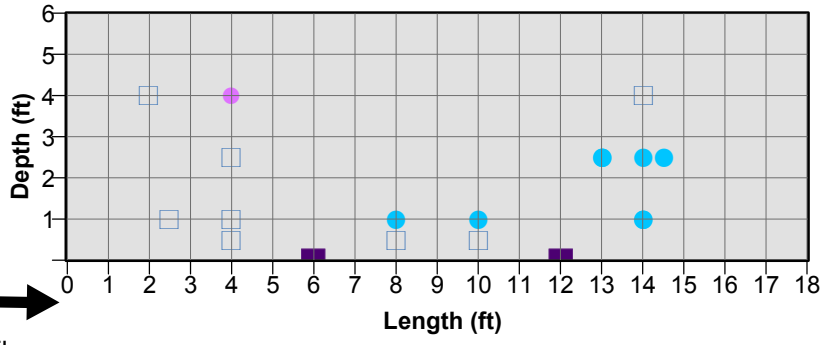
DNAPL PHASE EXPERIMENT
Chlorinated Ethenes + Ethene
October 4, 2002 (Day 42)
SERDP Hydrogen Biosparging Project

X-Z Plane (Y = 3.5 ft)

PCE

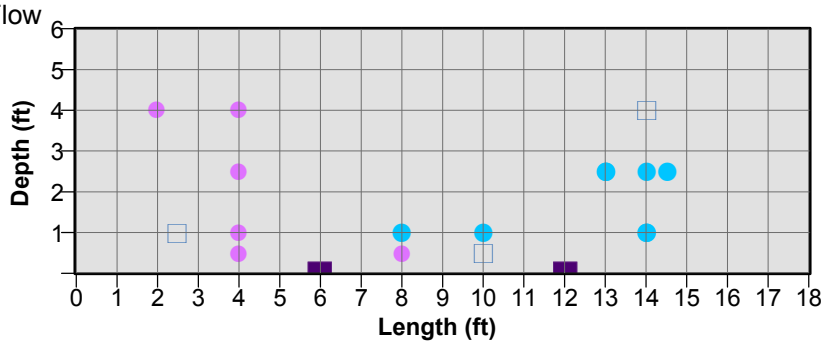


TCE

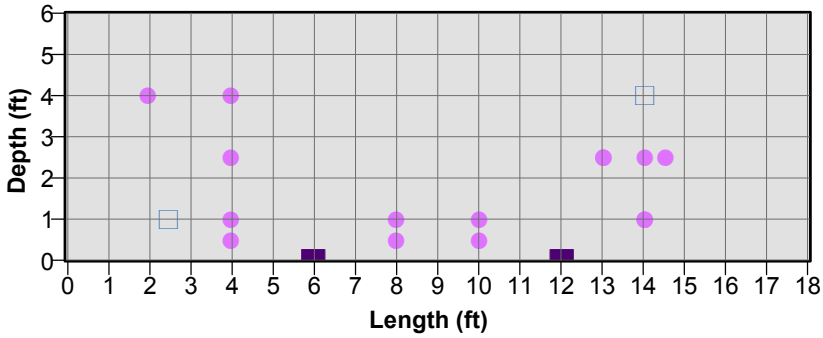


Water Flow

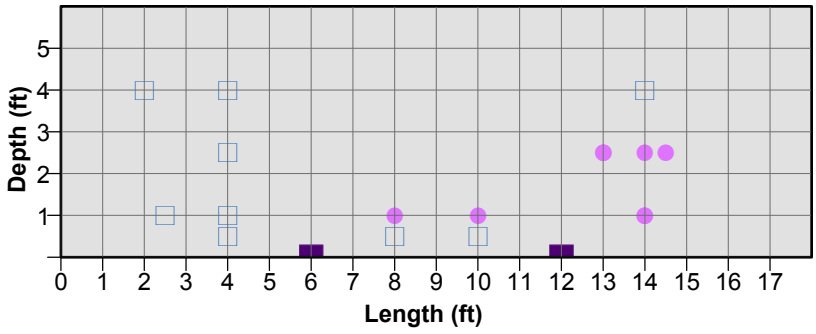
DCE



VC



Ethene



Legend

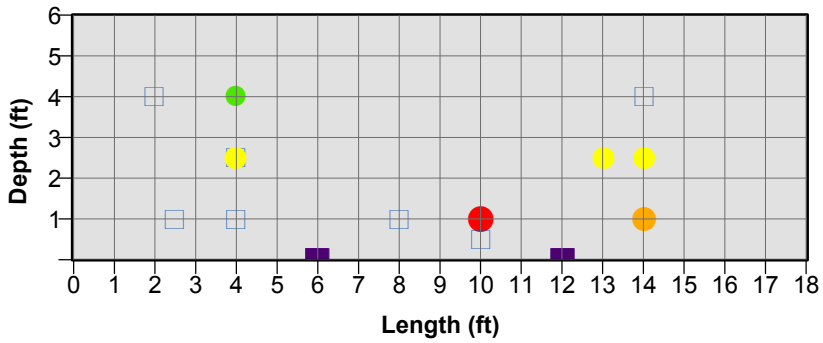
Concentration (uM)

- ND
- 0.001 - 0.1 uM
- >0.1 - 1.0 uM
- > 1 - 2 uM
- > 2 - 20 uM
- >20 - 100 uM
- > 100 - 300 uM
- > 300 - 1000 uM
- >1000 uM
- Sparge Point X-Z Plane

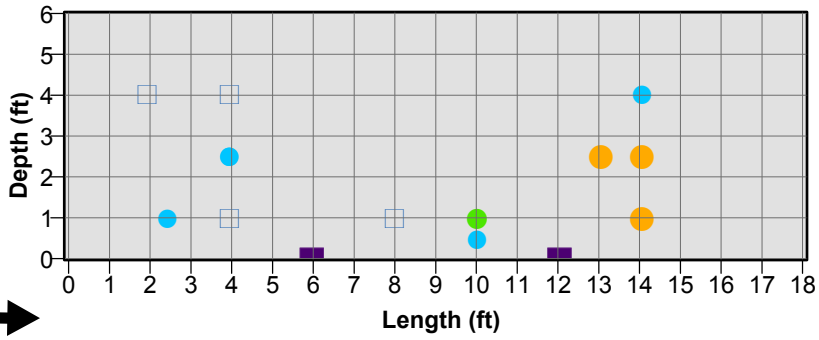
GROUNDWATER SERVICES, INC.	GSI Job No. G-2535-107	Drawn By: JJA	**DNAPL PHASE EXPERIMENT** **Chlorinated Ethenes + Ethene** **November 4, 2002 (Day 73)** **SERDP Hydrogen Biosparging Project**
	Issued: 7/16/03	Chk'd By: CEA	
	Revised: ---------	Aprv'd By: CEA	
	Scale: As Shown	**FIGURE E.4**	

X-Z Plane (Y = 3.5 ft)

PCE

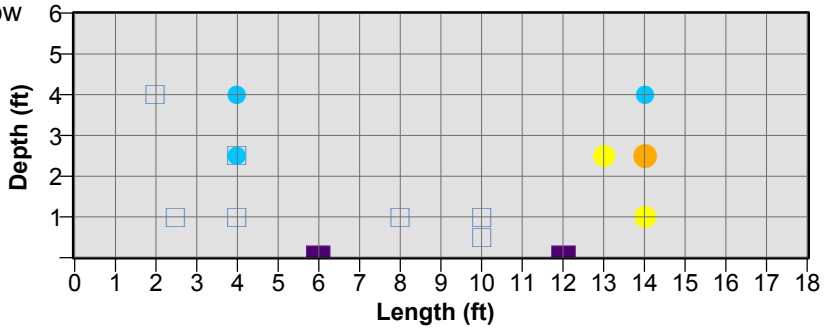


TCE

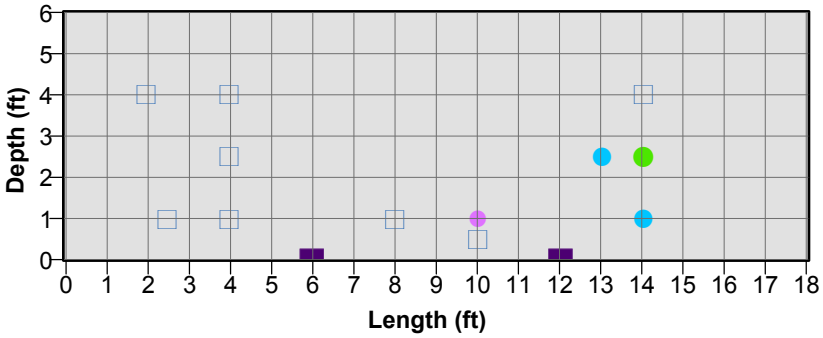


Water Flow

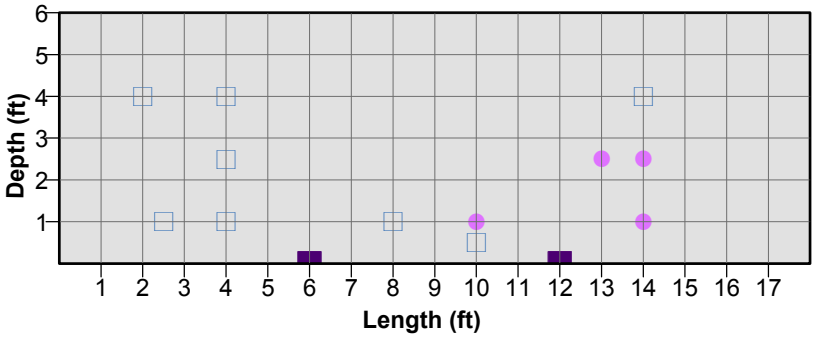
DCE



VC



Ethene



Legend

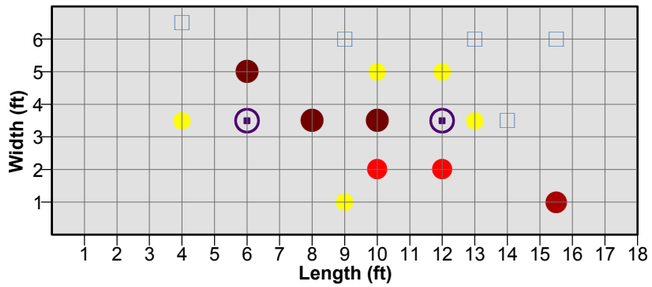
Concentration (uM)

- ND
- 0.001 - 0.1 uM
- >0.1 - 1.0 uM
- > 1 - 2 uM
- > 2 - 20 uM
- >20 - 100 uM
- > 100 - 300 uM
- > 300 - 1000 uM
- >1000 uM
- Sparge Point X-Z Plane

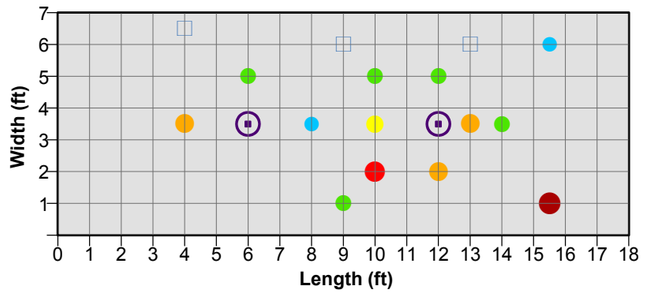
GROUNDWATER SERVICES, INC.	GSI Job No. G-2535-107	Drawn By: JJA	DNAPL PHASE EXPERIMENT Chlorinated Ethenes + Ethene December 5, 2002 (Day 104) SERDP Hydrogen Biosparging Project
	Issued: 7/16/03	Chk'd By: CEA	
	Revised: ---------	Aprv'd By: CEA	
	Scale: As Shown	FIGURE E.5	

X-Y Plane (Z = 2.5 ft)

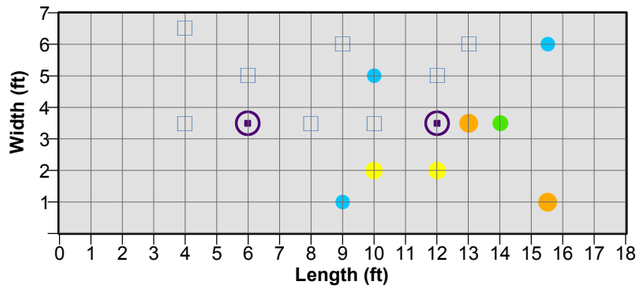
PCE



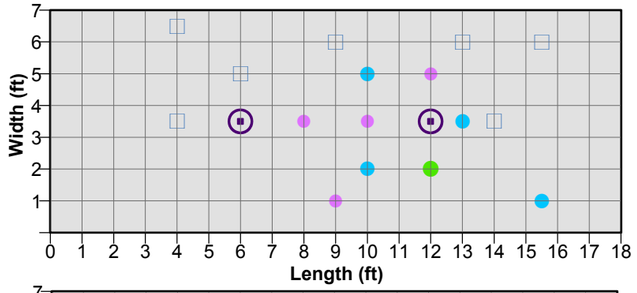
TCE



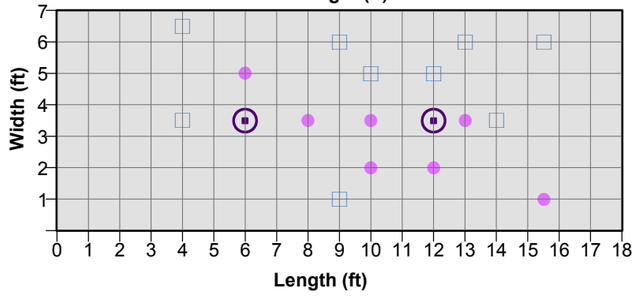
DCE



VC



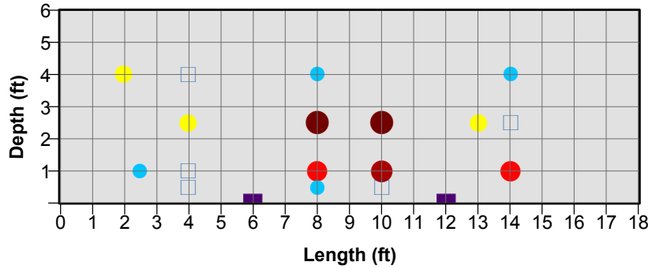
Ethene



Water Flow

X-Z Plane (Y = 3.5 ft)

PCE



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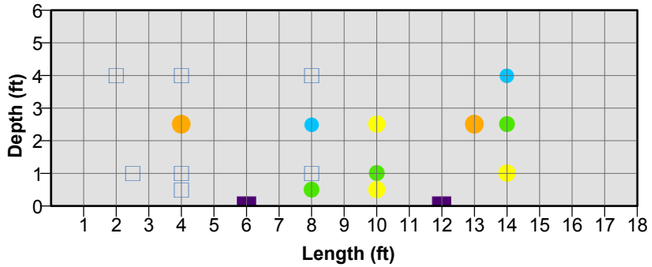
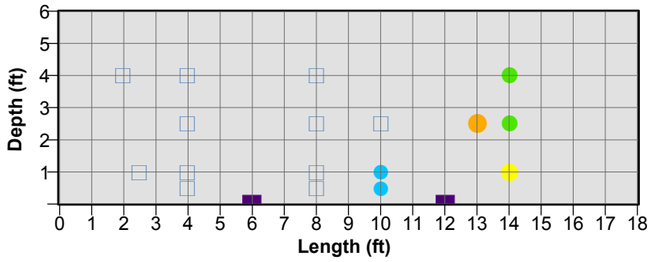
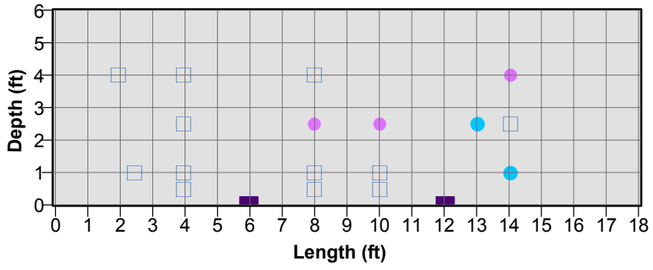


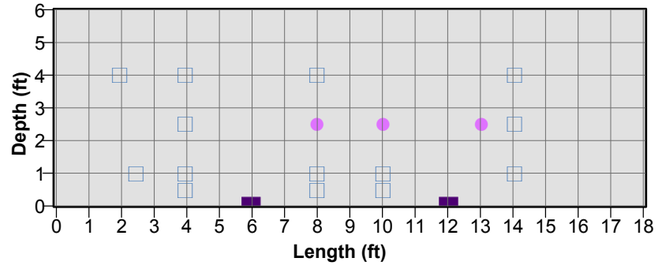
DCE



VC



Ethene



Legend

Concentration (uM)

- ND
- 0.001 - 0.1 uM
- >0.1 - 1.0 uM
- > 1 - 2 uM
- > 2 - 20 uM
- >20 - 100 uM
- > 100 - 300 uM
- > 300 - 1000 uM
- >1000 uM
- Sparge Point X-Z Plane
- Sparge Point X-Y Plane

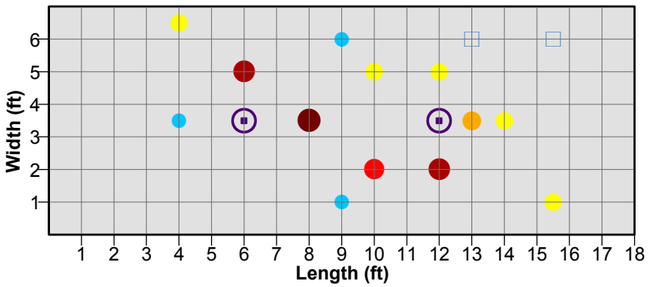
GROUNDWATER SERVICES, INC.

GSI Job No.	G-2535-107	Drawn By:	JJA
Issued:	7/16/03	Chk'd By:	CEA
Revised:	---------	Aprv'd By:	CEA
Scale:	As Shown	FIGURE E.6	

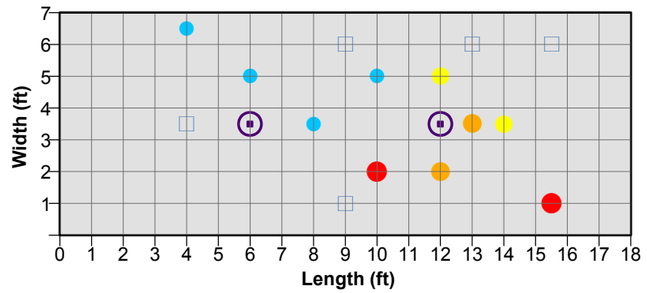
DNAPL PHASE EXPERIMENT
Chlorinated Ethenes + Ethene
January 9, 2003 (Day 139)
SERDP Hydrogen Biosparging Project

X-Y Plane (Z = 2.5 ft)

PCE

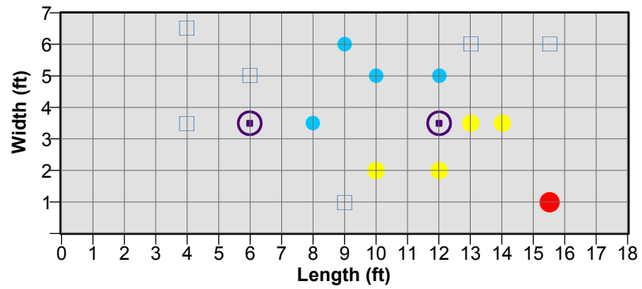


TCE

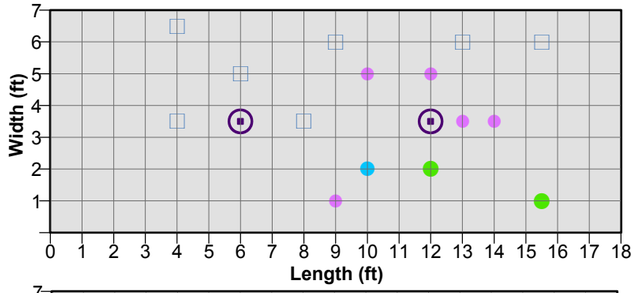


Water Flow

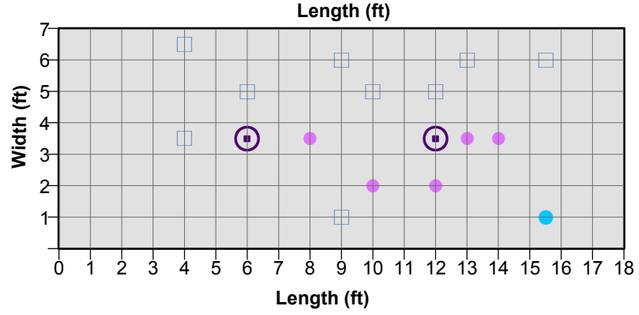
DCE



VC

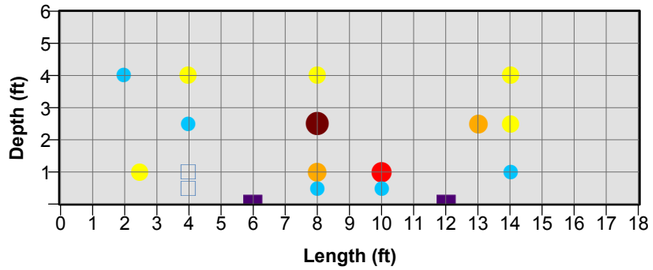


Ethene

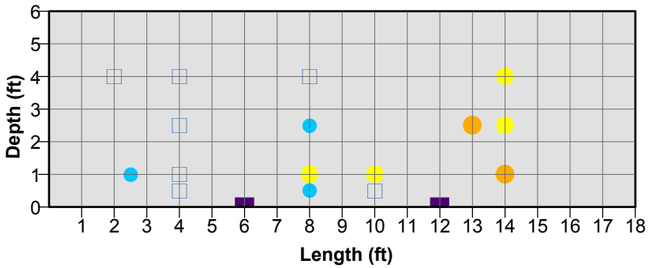


X-Z Plane (Y = 3.5 ft)

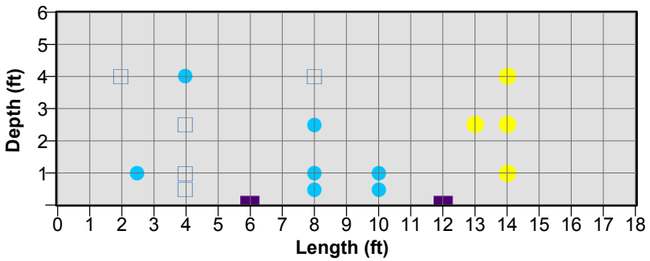
PCE



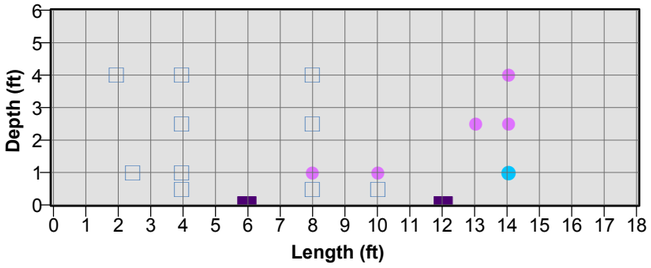
TCE



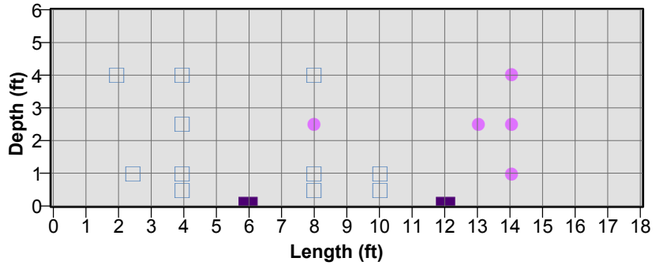
DCE



VC



Ethene



Legend

Concentration (uM)

- ND
- 0.001 - 0.1 uM
- >0.1 - 1.0 uM
- > 1 - 2 uM
- > 2 - 20 uM
- >20 - 100 uM
- > 100 - 300 uM
- > 300 - 1000 uM
- >1000 uM
- Sparge Point X-Z Plane
- Sparge Point X-Y Plane

GROUNDWATER SERVICES, INC.

GSI Job No.	G-2535-107	Drawn By:	JJA
Issued:	7/16/03	Chk'd By:	CEA
Revised:	---------	Aprv'd By:	CEA
Scale:	As Shown	FIGURE E.7	

DNAPL PHASE EXPERIMENT
Chlorinated Ethenes + Ethene
February 6 2003 (Day 167)
SERDP Hydrogen Biosparging Project

GSI Job No. G-2535
Issued: October 7, 2003

GROUNDWATER
SERVICES, INC.

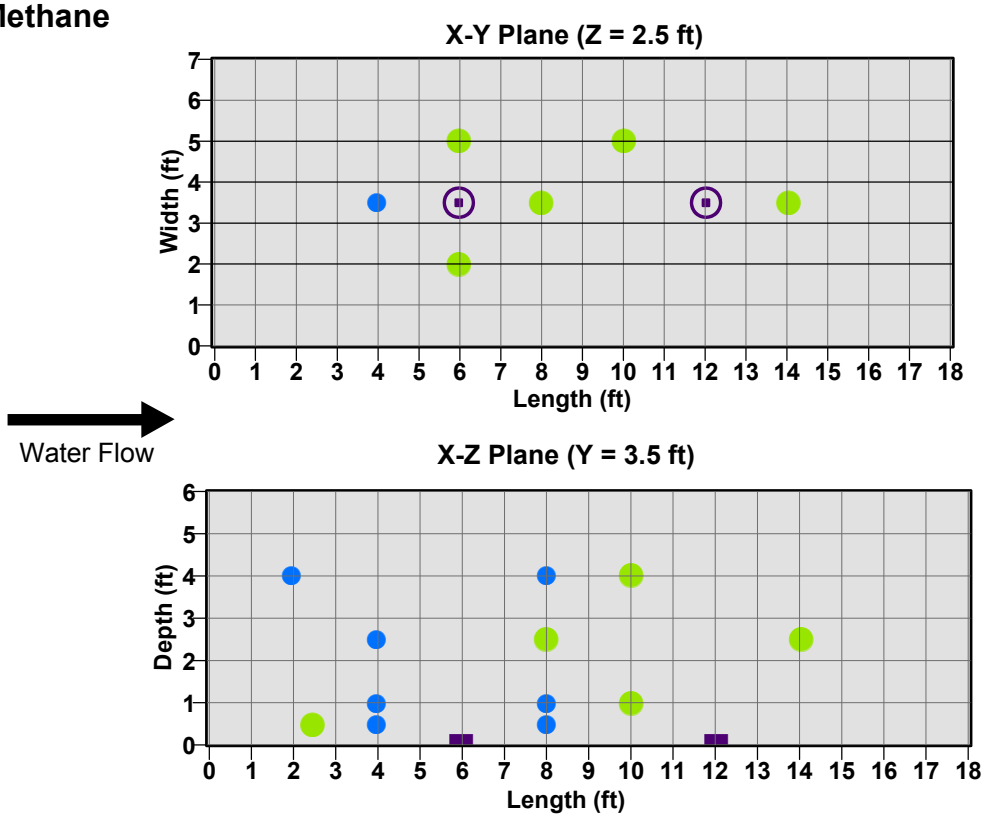
FINAL REPORT FOR LOW-VOLUME PULSED BIOSPARGING OF HYDROGEN FOR BIOREMEDIATION OF CHLORINATED SOLVENT PLUMES

Groundwater Services, Inc., Houston, TX

APPENDIX F:

Distribution of Methane and Acetate within the ECRS Tank
(DNAPL Experiment)

Methane

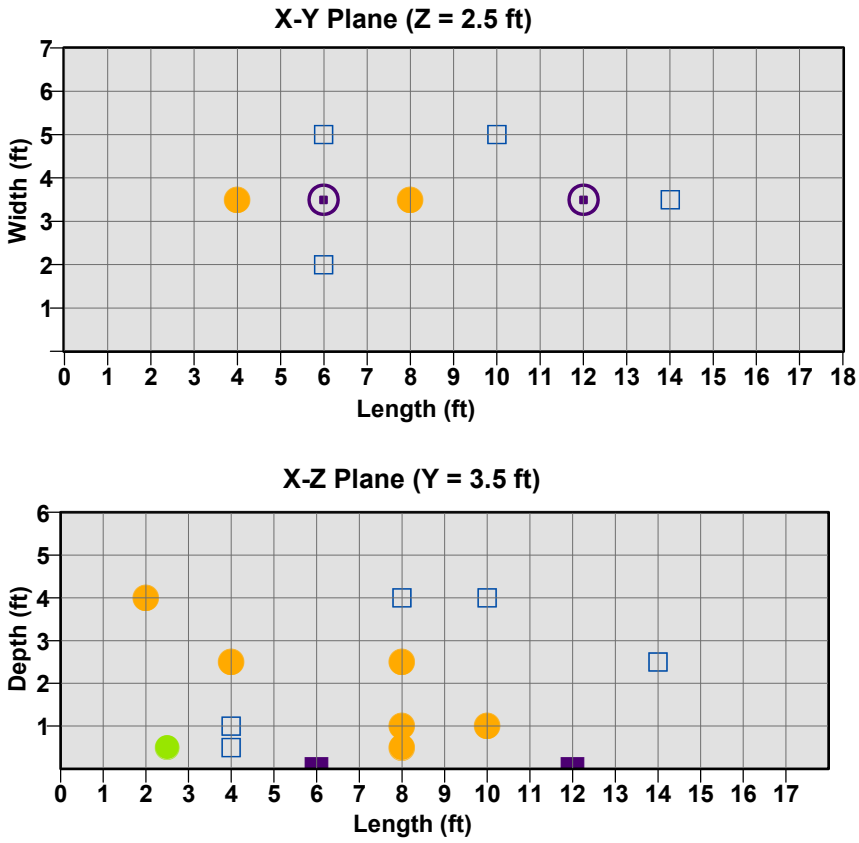


Legend

Methane Concentration

- ND
- <= 0.1 mg/L
- > 0.1 - 5.0 mg/L
- > 5.0 - 10.0 mg/L
- > 10.0 mg/L
- Sparge Point X-Y Plane
- Sparge Point X-Z Plane

Acetate



Legend

Acetate Concentration

- ND
- <= 0.1 mg/L
- > 0.1 - 10.0 mg/L
- > 10.0 - 50.0 mg/L
- > 50.0 mg/L
- Sparge Point X-Y Plane
- Sparge Point X-Z Plane

GROUNDWATER SERVICES, INC.

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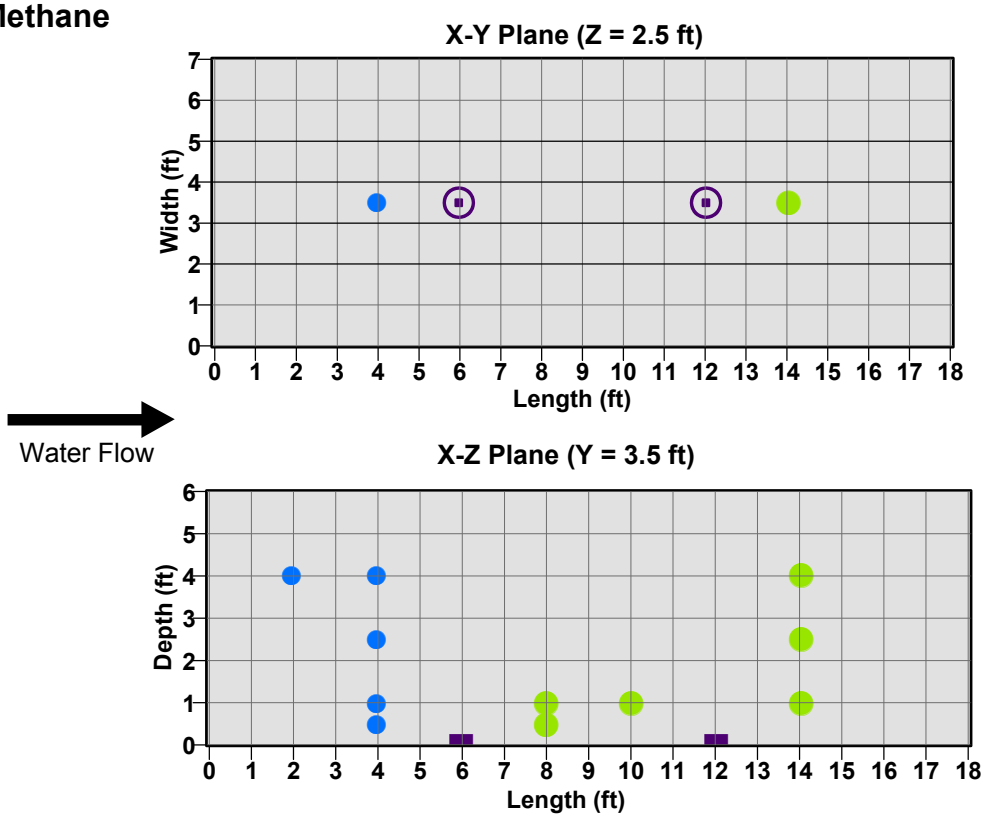
Scale:	As Shown	FIGURE F.1	

DNAPL Phase Experiment
Methane and Acetate
August 23, 2002
(Before DNAPL Addition)
SERDP Hydrogen Biosparging Project

Methane

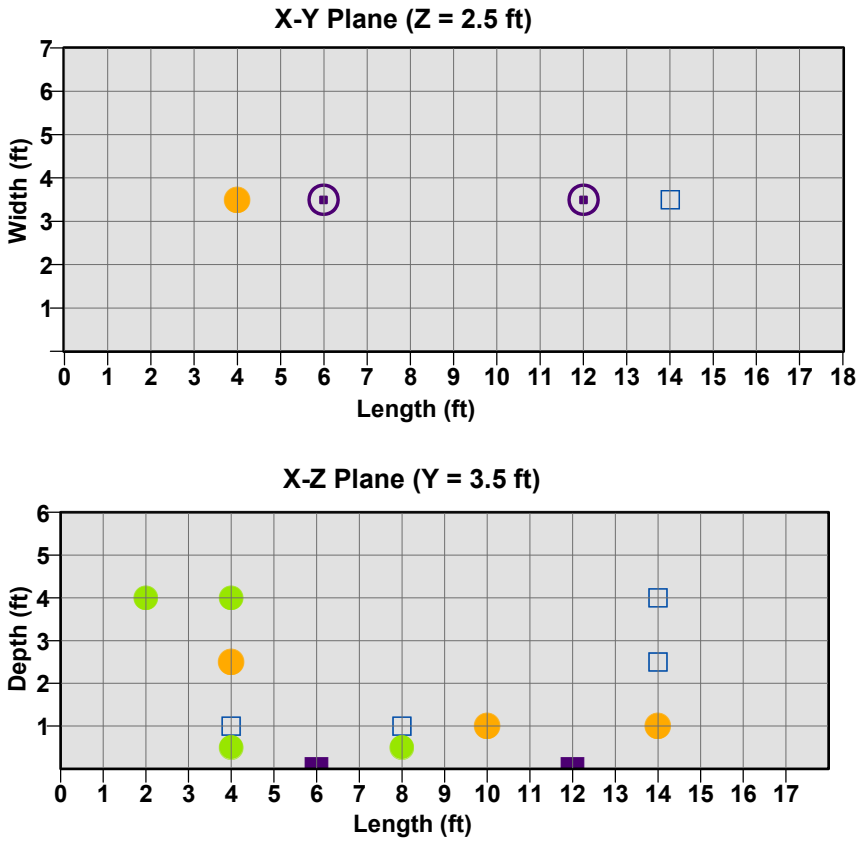


Legend

Methane Concentration

- ND
- <= 0.1 mg/L
- > 0.1 - 5.0 mg/L
- > 5.0 - 10.0 mg/L
- > 10.0 mg/L
- Sparge Point X-Y Plane
- Sparge Point X-Z Plane

Acetate



Legend

Acetate Concentration

- ND
- <= 0.1 mg/L
- > 0.1 - 10.0 mg/L
- > 10.0 - 50.0 mg/L
- > 50.0 mg/L
- Sparge Point X-Y Plane
- Sparge Point X-Z Plane

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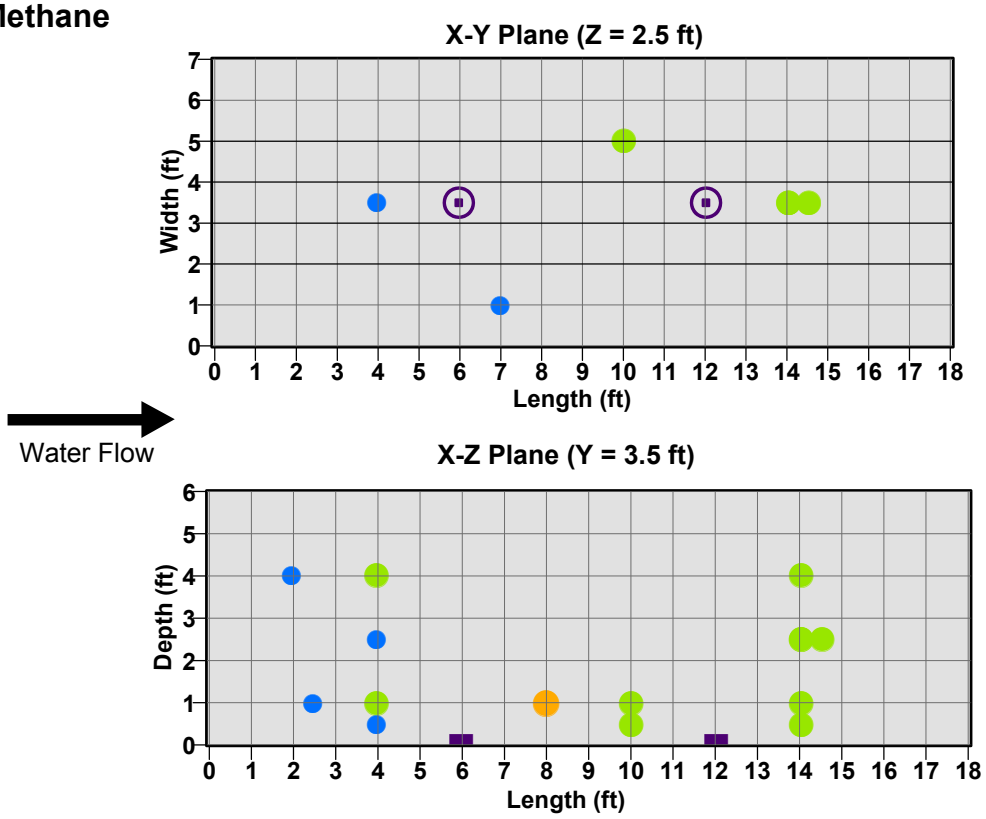
Scale:	As Shown	FIGURE F.2	

DNAPL Phase Experiment
Methane and Acetate
September 6, 2002 (Day 17)
SERDP Hydrogen Biosparging Project

Methane

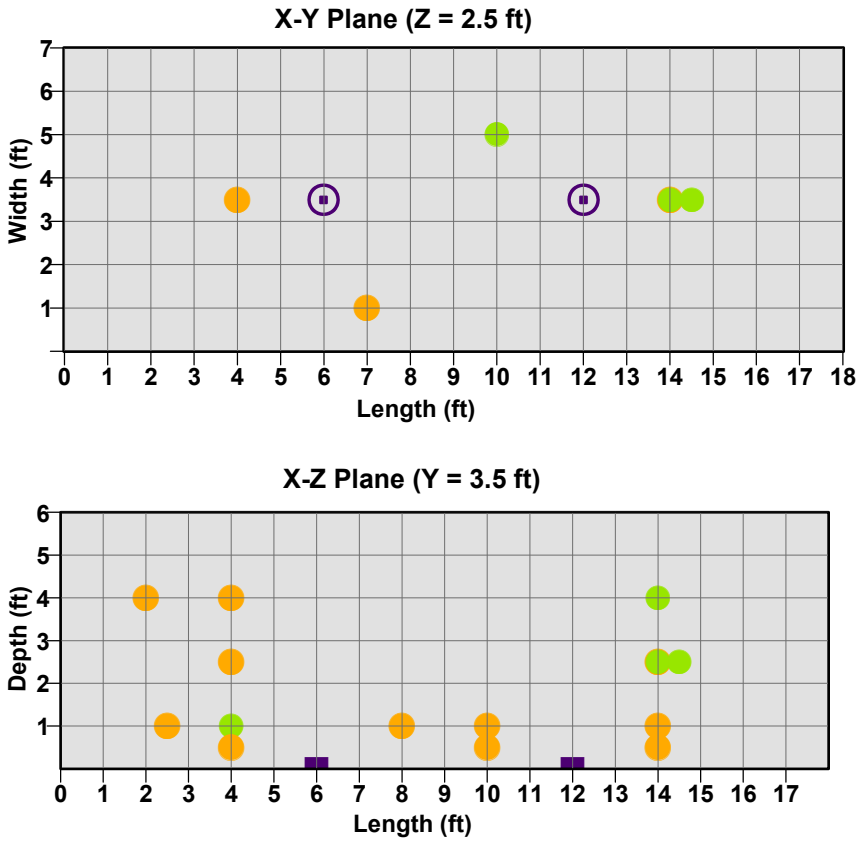


Legend

Methane Concentration

- ND
- <= 0.1 mg/L
- > 0.1 - 5.0 mg/L
- > 5.0 - 10.0 mg/L
- > 10.0 mg/L
- Sparge Point X-Y Plane
- Sparge Point X-Z Plane

Acetate



Legend

Acetate Concentration

- ND
- <= 0.1 mg/L
- > 0.1 - 10.0 mg/L
- > 10.0 - 50.0 mg/L
- > 50.0 mg/L
- Sparge Point X-Y Plane
- Sparge Point X-Z Plane

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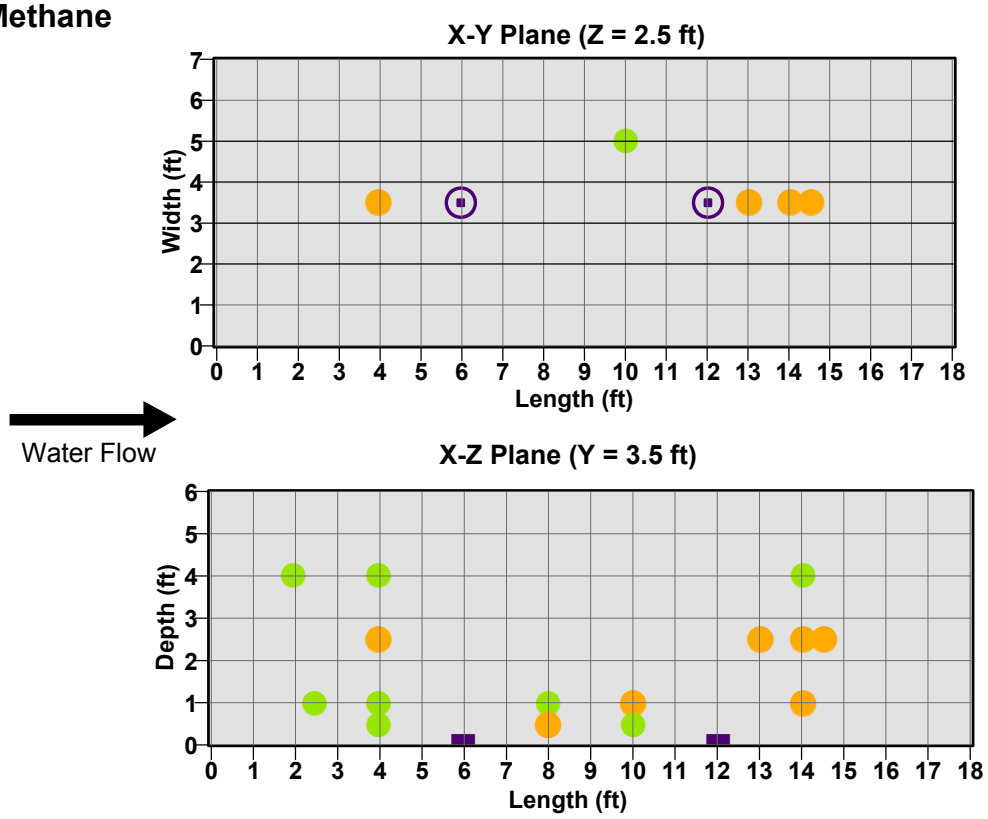
Scale:	As Shown	FIGURE F.3	

DNAPL Phase Experiment
Methane and Acetate
October 4, 2002 (Day 42)
SERDP Hydrogen Biosparging Project

Methane

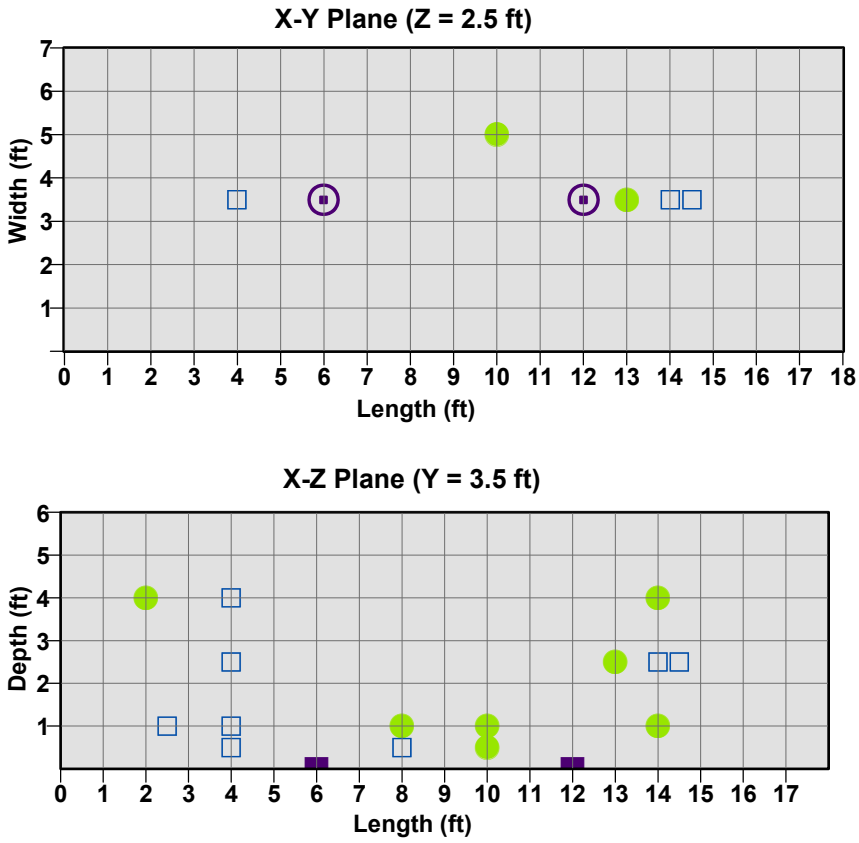


Legend

Methane Concentration

- ND
- <= 0.1 mg/L
- > 0.1 - 5.0 mg/L
- > 5.0 - 10.0 mg/L
- > 10.0 mg/L
- Sparge Point X-Y Plane
- Sparge Point X-Z Plane

Acetate



Legend

Acetate Concentration

- ND
- <= 0.1 mg/L
- > 0.1 - 10.0 mg/L
- > 10.0 - 50.0 mg/L
- > 50.0 mg/L
- Sparge Point X-Y Plane
- Sparge Point X-Z Plane

GROUNDWATER SERVICES, INC.

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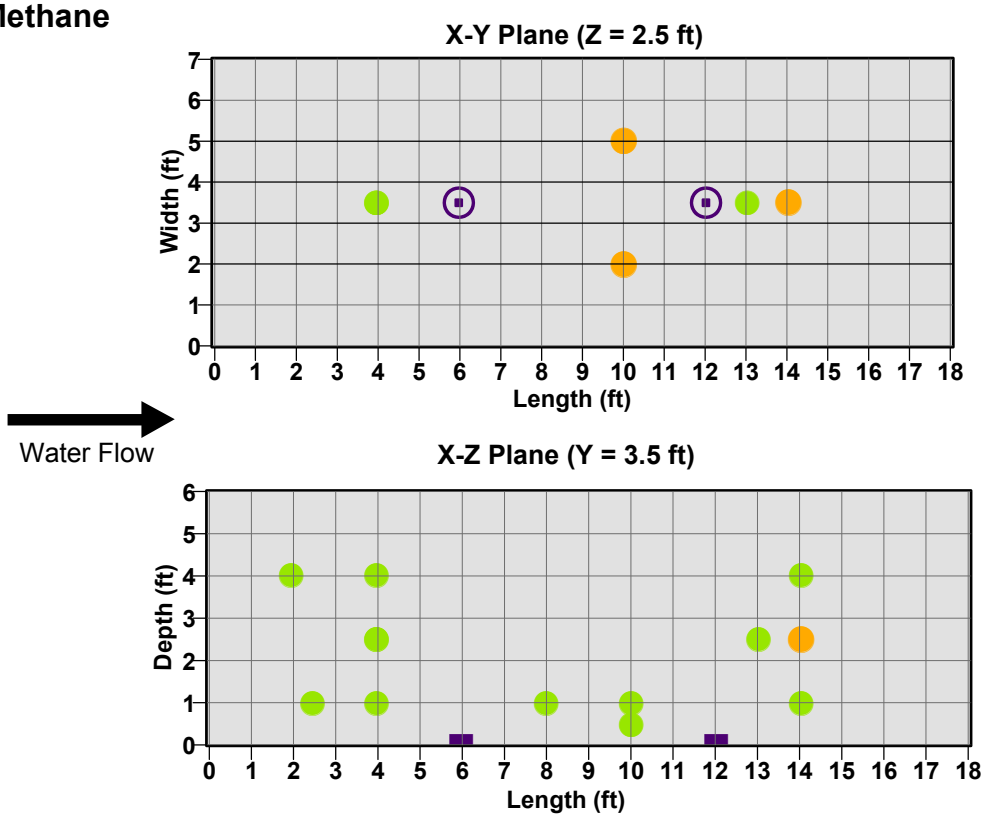
Scale:	As Shown	FIGURE F.4	

DNAPL Phase Experiment
Methane and Acetate
November 4, 2002 (Day 73)
SERDP Hydrogen Biosparging Project

Methane

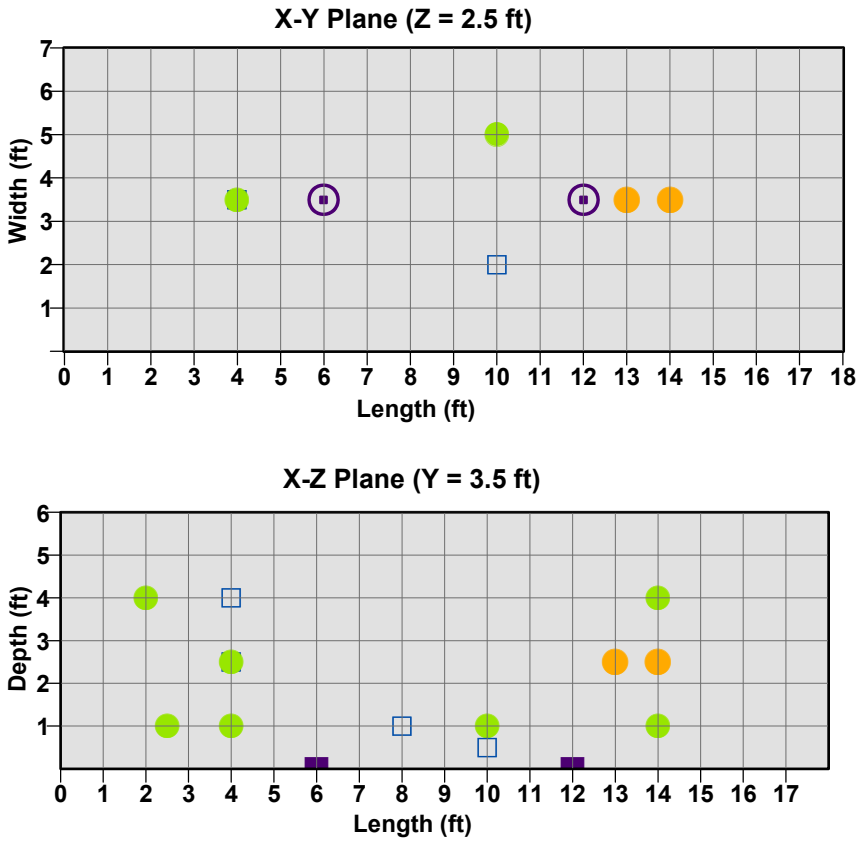


Legend

Methane Concentration

- ND
- <= 0.1 mg/L
- > 0.1 - 5.0 mg/L
- > 5.0 - 10.0 mg/L
- > 10.0 mg/L
- Sparge Point X-Y Plane
- Sparge Point X-Z Plane

Acetate



Legend

Acetate Concentration

- ND
- <= 0.1 mg/L
- > 0.1 - 10.0 mg/L
- > 10.0 - 50.0 mg/L
- > 50.0 mg/L
- Sparge Point X-Y Plane
- Sparge Point X-Z Plane

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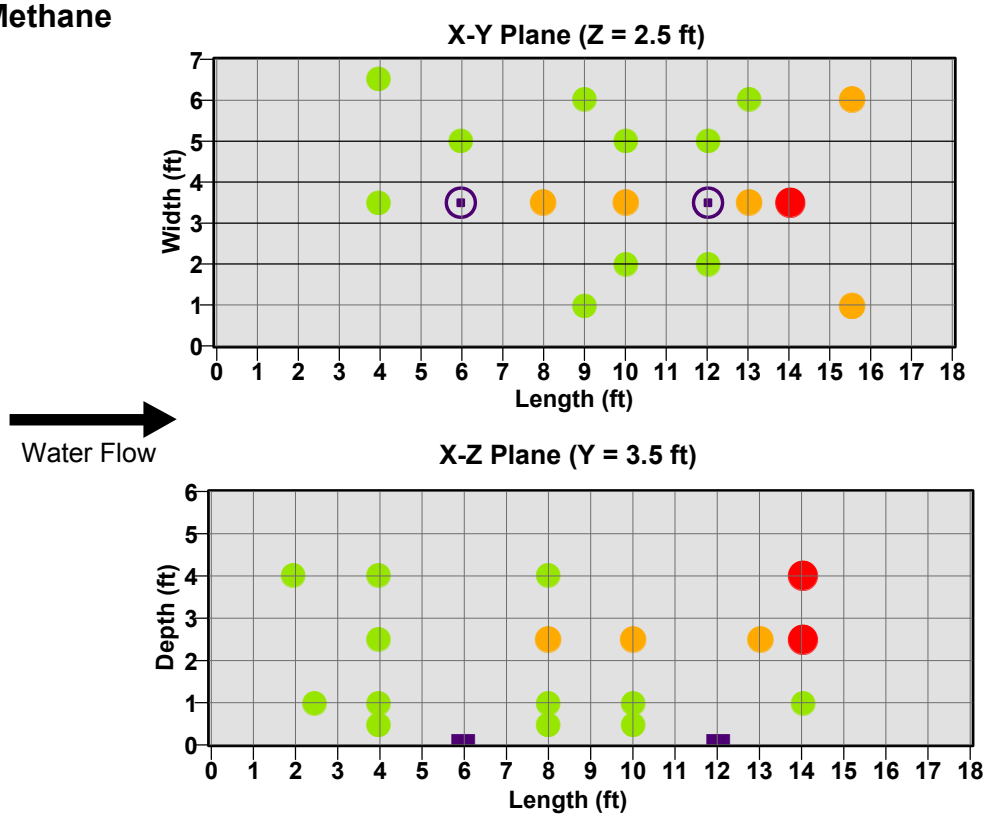
Revised:	---------	Aprv'd By:	CEA
Scale:	As Shown	FIGURE F.5	

DNAPL Phase Experiment
Methane and Acetate
December 5, 2002 (Day 104)
SERDP Hydrogen Biosparging Project

Methane

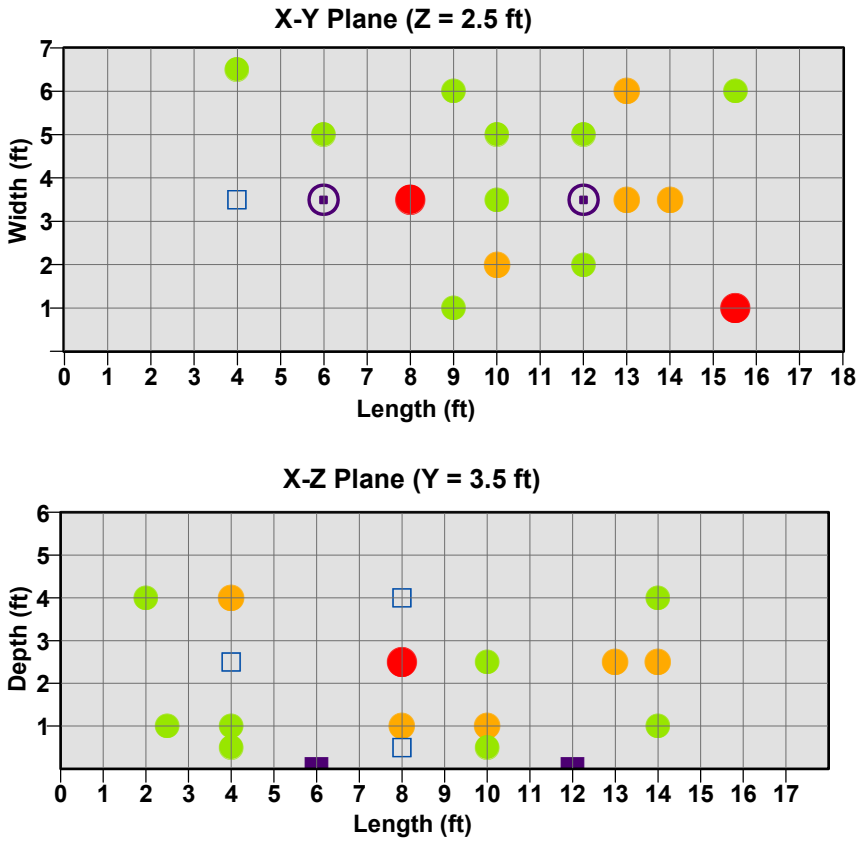


Legend

Methane Concentration

- ND
- <= 0.1 mg/L
- > 0.1 - 5.0 mg/L
- > 5.0 - 10.0 mg/L
- > 10.0 mg/L
- Sparge Point X-Y Plane
- Sparge Point X-Z Plane

Acetate



Legend

Acetate Concentration

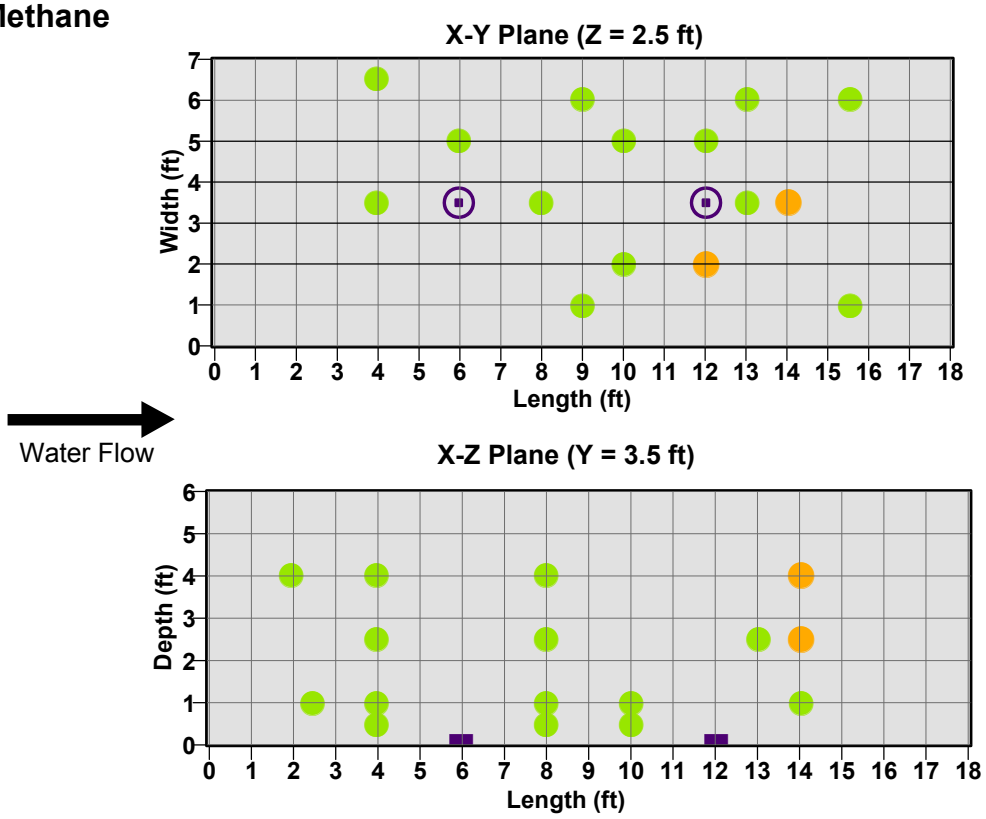
- ND
- <= 0.1 mg/L
- > 0.1 - 10.0 mg/L
- > 10.0 - 50.0 mg/L
- > 50.0 mg/L
- Sparge Point X-Y Plane
- Sparge Point X-Z Plane

GROUNDWATER SERVICES, INC.

GSI Job No.	G-2535-107	Drawn By:	JJA
Issued:	7/16/03	Chk'd By:	CEA
Revised:	---------	Aprv'd By:	CEA
Scale:	As Shown	FIGURE F.6	

DNAPL Phase Experiment
Methane and Acetate
January 9, 2003 (Day 139)
SERDP Hydrogen Biosparging Project

Methane

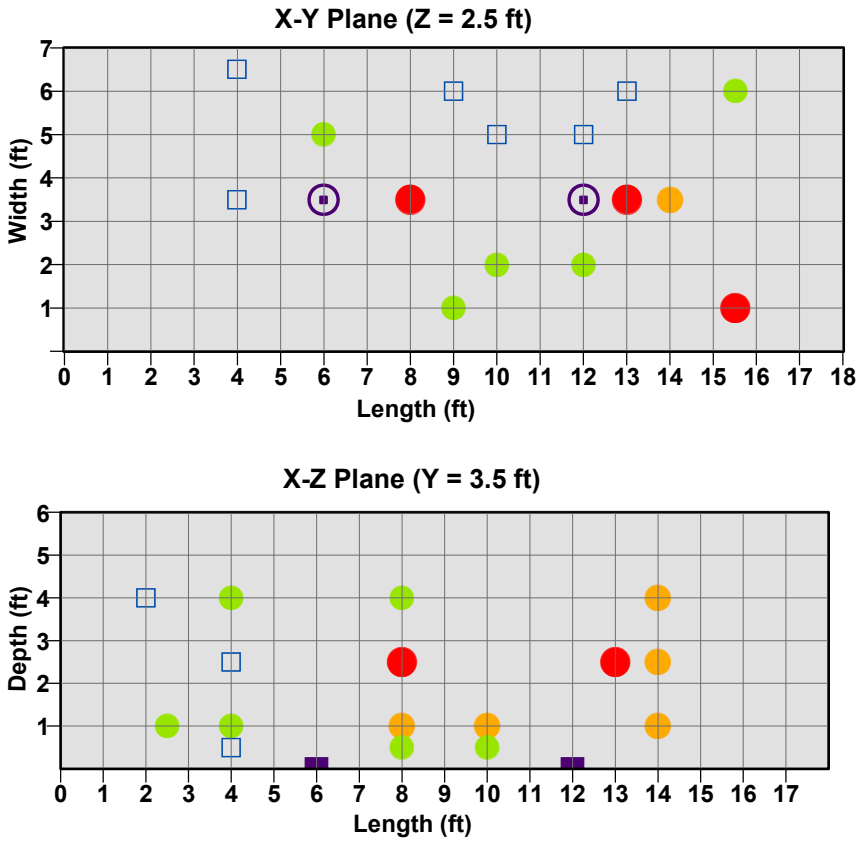


Legend

Methane Concentration

- ND
- <= 0.1 mg/L
- > 0.1 - 5.0 mg/L
- > 5.0 - 10.0 mg/L
- > 10.0 mg/L
- Sparge Point X-Y Plane
- Sparge Point X-Z Plane

Acetate



Legend

Acetate Concentration

- ND
- <= 0.1 mg/L
- > 0.1 - 10.0 mg/L
- > 10.0 - 50.0 mg/L
- > 50.0 mg/L
- Sparge Point X-Y Plane
- Sparge Point X-Z Plane

GROUNDWATER SERVICES, INC.

GSI Job No.	G-2535-107	Drawn By:	JJA
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Revised:	---------	Aprv'd By:	CEA
Scale:	As Shown	FIGURE F.7	

DNAPL Phase Experiment
Methane and Acetate
February 6, 2003 (Day 167)
SERDP Hydrogen Biosparging Project